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THE NATURAL BETA-RAY SPECTRUM OF RaD*

By L. F. Curtiss+

Abstract

The natural β-ray spectrum of RaD has been photographed and the energies of its lines directly compared with those of the RaB β-ray spectrum in the same region. The RaB line $H\rho = 660.9$ as measured by Ellis and Skinner[1] has been taken as a standard reference line. The following values for the energies of the lines have been determined:

No.	Intensity	$H\rho$	Energy (volts$\times 10^{-6}$)
1	50	594.3	0.3033
2	3	600.3	0.3092
3	25	709.1	0.4268
4	10	735.2	0.4576
5	1	742.5	0.4663

No. 5 is a line which has previously escaped detection. The analysis of this spectrum for determining the energy of the γ-ray responsible for it shows conclusively that the γ-ray is emitted *after* the disintegration. This is in accord with Meitner's[2] view. The energy of the γ-ray is determined as 0.467×10^6 volts.

Introduction

THE present interpretation of β-ray spectra has led to two views regarding the emission of the γ-ray. Ellis[3] originally contended that the γ-ray was emitted before the disintegration, i.e., before the emission of the nuclear or primary β-ray. On his view of course the secondary β-rays should have energies related to the energy levels of the atom before disintegration. Meitner,[2] on the other hand, concluded that the γ-radiation follows the disintegration and is a direct result of the disturbance of the nuclear levels occasioned by the ejection of the primary β-ray and the transition from one nuclear system to the other.

The settlement of this question is important. However, the experi-

* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

+ National Research Council Fellow.

[1] C. D. Ellis and H. W. B. Skinner, Proc. Roy. Soc. **105**, 165 (1924).

[2] L. Meitner, Zeits. f. Physik **11**, 35, (1922).

[3] C. D. Ellis, Proc. Cam. Phil. Soc. **21**, 121 (1922).

mental material which throws definite light on the problem is still very meager. In the majority of cases the measurements of β-ray spectra may be interpreted in terms of either hypothesis. This ambiguity arises from the nature of the β-ray spectrum. The accepted interpretation of the β-ray line spectra is that the lines represent groups of electrons which have been ejected from the x-ray levels of the atom by γ-radiation from the nucleus of the atom itself. The velocities of these electron groups are measured by bending them in a uniform magnetic field. The velocity is proportional to the product $H\rho$, where H is the intensity of the magnetic field, and ρ the radius of the circle on which the β-particles travel. For the harder β-radiation of RaB and for all lines in the RaC β-ray spectrum, the observed $H\rho$ should differ by less than one-half percent if the atomic levels for $Z=83$ were used instead of those for $Z=82$. (Since RaB is an isotope of lead and disintegrates into RaC, an isotope of bismuth, these are the two atomic systems with which we are concerned in this case.) This difference is beyond the limit of accuracy of most experiments. However, Ellis and Skinner[1] in their more precise measurements of the RaB β-ray spectrum, find that in the "*C*" region they are forced to use atomic levels for $Z=83$ instead of 82 in order to obtain agreement for the energy of the γ-ray. This is the most decisive previous evidence in favor of Meitner's hypothesis.

It is clear that further evidence on this question can be obtained by studying other radioactive elements which emit comparatively soft γ-radiation. Under such circumstances the secondary electrons of the β-ray spectrum will have lower velocities and therefore energies more nearly comparable with the energies of the atomic levels. The natural β-ray spectrum of RaD is well suited to this purpose. RaD is an isotope of RaB and emits a single γ-ray of energy considerably less than that corresponding to the K limit for this atom. Consequently its β-ray spectrum contains electrons from the L level and levels of lower energy. Numerous measurements have been made of this spectrum but there is still great divergence of opinion concerning it. Various observers disagree even on the number of lines that it contains. For example, Ellis[3] observed five lines whereas Meitner[2] later found but three. For convenience previous results are tabulated below. The quantities given under the name of each author are the values of $H\rho$ for lines which they observed in the RaD β-ray spectrum.

The weight of evidence favors a β-ray spectrum of four lines, as originally reported by Danysz. The most recent measurements are by

TABLE I

Hρ values of RaD β-ray spectrum by previous investigators

Danysz[4]	Ellis[3]	Meitner[2]	Black[5]
602	600	602	600
607	605	—	606
—	628	—	—
718	717	718	714
743	742	741	738

Black.[5] These differ from Danysz's by an approximately proportional decrease of the energy of all lines. The failure of certain investigators to detect some of these lines has given rise to considerable discussion regarding their physical significance.[2]

EXPERIMENTAL RESULTS

With the hope of throwing further light on the problem of the emission of the γ-ray, I have taken a number of photographs of the RaD β-ray spectrum. The spectrograph was of the usual type, but with large dispersion ($\rho_{max}=7.5$ cm). The magnet was one specially designed for the study of β-ray spectra. It has poles 24 cm in diameter and gives a field uniform to one part in 2000 by actual measurement over a circle 15 cm in diameter. This magnet and the spectrograph will be fully described elsewhere.[6] The magnet was excited by an independent set of storage batteries. The current was measured and controlled by a Leeds & Northrup potentiometer and standard resistance in the usual manner. It was found comparatively easy to maintain the current constant to at least one part in 2000 over long periods of time. In order to avoid the trouble of precise absolute measurement of the intensity of the magnetic field, comparison photographs of RaB lines in the same region were made. The line $H\rho=660.9$, as measured by Ellis and Skinner,[1] was used as a reference line and their value for its energy was accepted as a standard. The lines of the RaD spectrum here reported have thus been measured in terms of this value. It is obvious that the absolute energies of the lines observed here must be as accurate as this value, since a direct comparison of this kind can be made with great precision. Eastman x-ray plates were found at least 50 percent more sensitive than ordinary plates to β-radiation in this region. This test was made by exposing a plate of each kind simultaneously in the spectrograph and developing the two plates

[4] Danysz, Le Radium **10**, 4 (1913).
[5] Black, Proc. Roy. Soc. **109**, 166 (1925).
[6] L. F. Curtiss, J.O.S.A. and R.S.I. in press.

together. Consequently all exposures were made with x-ray plates. The RaD sources were obtained by the anodic deposition on a fine platinum wire in the usual way. Two different preparations of RaD were used, both giving identical results.

The experiments were carried out as follows: The current through the magnet was adjusted to the desired value and after several reversals the switch was thrown to the "direct" position. A source of RaD was inserted into the spectrograph by means of a ground glass joint, the photographic plate having been previously put in position. The spectrograph was then exhausted by a large diffusion pump. A shutter, manipulated by a ground glass joint, protected the plate from β-radiation during the period of exhaustion, which usually was of the order of 20 minutes. After a sufficient exposure the shutter was closed, air admitted, the spectrograph opened, and the plate removed. A fresh plate was then inserted. The RaD source was replaced by a source consisting of the active deposit of radon and a new exposure made. Throughout this time the current through the magnet was maintained constant at its original value with a high degree of accuracy. Thus the second exposure gave the β-ray spectrum of RaB in the same magnetic field. A fiducial mark put on the plate while still in the spectrograph permitted the determination of its position relative to the apparatus. Several experiments were performed in this manner. The measurements on all plates agreed with each other to at least one part in 1000. The results are tabulated below.

TABLE II

$H\rho$ and energy values of RaD β-ray spectrum

No.	$H\rho$	Intensity	Energy (volts$\times 10^{-6}$)
1	594.3	50	0.3033
2	600.3	3	0.3092
3	709.1	25	0.4268
4	735.2	10	0.4576
5	742.5	1	0.4663

The first four lines given above are those originally reported by Danysz in 1913, but the $H\rho$ values and the energies are considerably lower. In addition a faint line of higher energy has been observed which has previously escaped detection. This line appeared on all plates and there is no doubt of its existence, although it is too faint to measure with the same accuracy as the other lines. The value here given was determined from measurements of the plates independently by Mr. R. L. Chenault and by myself. As can be seen from the photographic reproductions, Plate I, there is no trace of the line $H\rho = 628$ reported by Ellis. A careful scrutiny of all plates failed to reveal it. The line $H\rho = 600.3$ (No. 2 in Table II) is clearly visible even in the

photographic reproduction although Meitner failed to detect it. This failure was presumably due to the low dispersion with which she worked. The photographs reproduced in this paper are about one and a half times actual size, and illustrate the dispersion employed. *A* is a reproduction of one of the spectrograms for RaD and *B* shows the comparison spectrum of RaB.

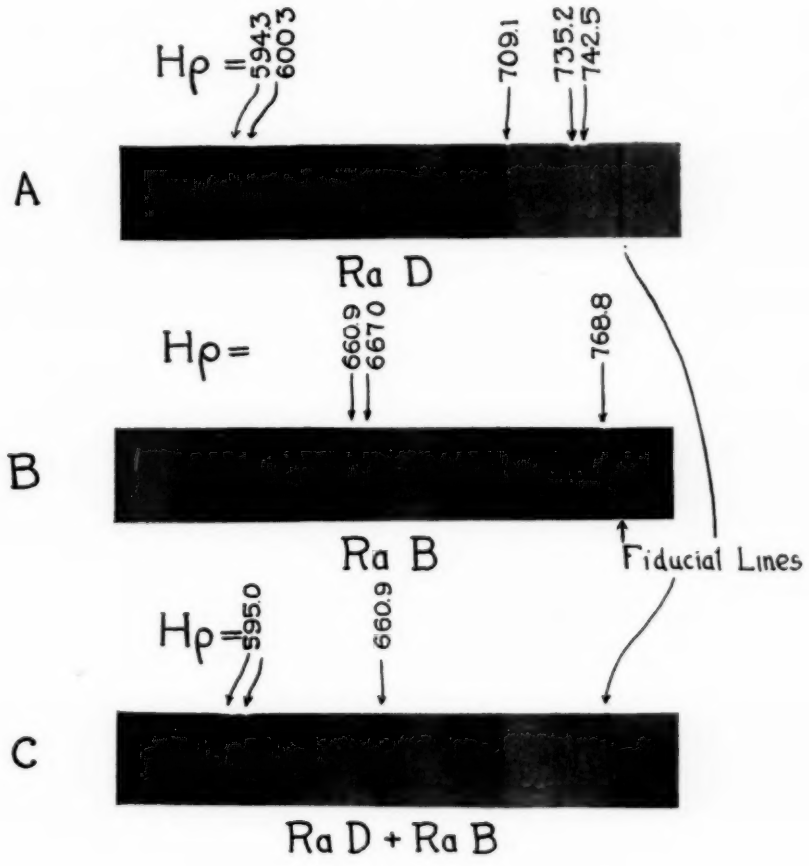

Plate I. Beta-ray spectra of RaD and RaB.

Since the values given in Table II differ consistently by at least one percent from the best previous measurements, a control experiment was considered necessary. The only objectionable feature of the foregoing procedure is the necessity for removing both plate and source between the RaD exposure and the calibration exposure with RaB. It would be much better to obtain the calibration simultaneously with the RaD exposure. Obviously only one line in the one spectrum need

be checked against a corresponding line in the other. To this end the fine platinum wire on which the RaD had been deposited was exposed in radon in the usual way and activated with RaB. The wire was then placed in the spectrograph and the two spectra obtained on one plate by the single exposure. The measurements of this plate follow:

	ρ(observed)	$H\rho$	
RaB	6.365 cm	660.9	(Ellis and Skinner)
RaD	5.733 cm	595.0	(calculated)

These lines selected for comparison are the strongest lines in this region of each spectrum. As the above table indicates, the calculated value of $H\rho$ for the RaD lines is 595.0, in good agreement with 594.3 obtained from the first series of experiments. This combination photograph is reproduced in Plate IC.

The importance of the new line $H\rho = 742$ becomes evident when we consider the energy of the γ-ray responsible for this β-ray spectrum. Table III gives the energies corresponding to the observed $H\rho$ values. These energies, increased by the energy of the appropriate x-ray level as indicated, are computed for $Z = 82$ and 83.

TABLE III

Energy of γ-ray from RaD

		$Z=82$		$Z=83$	
$H\rho$	Energy (volts$\times 10^5$)	Level of origin	Energy of γ-ray (volts$\times 10^{-5}$)	Level of origin	Energy of γ-ray (volts$\times 10^{-5}$)
594.3	0.3033	L_{I}	0.4617	L_{I}	0.4669
600.3	0.3092	L_{II}	0.4612	L_{II}	0.4663
709.1	0.4268	M_{II}	0.4623	M_{I}	0.4668
735.2	0.4576	N_{III}	0.4643	N_{I}	0.4672
742.5	0.4663	——	0.4663	——	0.4663

The levels for atomic number 82 have been selected to give the best possible agreement, leaving all other considerations aside. Even so, the agreement is very poor. To secure approximate constancy for the energy of the γ-ray, it has been necessary to omit the M_{I} level and retain the M_{II} level. In the N group only the N_{III} level can be used. Such procedure is contrary to the weight of evidence of all observers in this field. It is now a well established fact that under the conditions here considered the levels will be present in the β-ray spectrum with intensities in the order of their binding energy. If we adhere to this principle, there is no agreement whatever. The newly observed line has an energy of 0.4663 times 10^5 volts. However, the best estimate of the energy of the γ-ray as deduced from the levels of $Z = 82$ in the above table is 0.462 times 10^5 volts. This involves the obvious paradox of a γ-ray causing the emission of β-radiation of still greater energy. It should be noted that the energy of the new β-ray line is more than

one percent higher than that deduced for the γ-ray. This difference cannot be attributed to experimental error.

The last column of the table shows the excellent agreement obtained for the energy of the γ-ray when the levels for $Z=83$ are used. The energy is constant to one part in 500. Furthermore the intensities from the various levels follow in the order to be anticipated. Now the M_{I} level and the N_{I} level fit perfectly. No level is assigned to the new line since it is already approximately equal to the energy deduced for the γ-ray. The simplest explanation of this apparent equality is that this line represents particles ejected from the outer levels of the atom where the binding energy is relatively insignificant. The intensity favors this explanation very strongly. The other alternative is to accept Meitner's hypothesis that some at least of the primary β-radiation from the nucleus should escape with energy exactly equal to that of the γ-ray. However, the reason for such an assumption is not altogether clear. Furthermore, the intensity of this line does not agree with such an interpretation. This is discussed below.

The excellent agreement obtained for the various levels for atomic number 83 is in itself a strong argument for assuming that the γ-ray ejected the electrons in the β-ray spectrum from the levels of this atom. This means that the γ-ray is emitted after the emission of the primary β-particle when the electrons have adjusted themselves to their new energies. The fact that no agreement whatever can be obtained with the line $H\rho=742$ on the basis of the levels of atomic number 82 reinforces this argument most decidedly. Consequently it is safe to conclude that the γ-ray is emitted after disintegration in accord with Meitner's view.

The interesting question arises as to what becomes of the primary β-radiation. Ellis in his interpretation accounted for this radiation in the continuous spectrum. But he supposed the primary radiation to come after the emission of the γ-ray. Under these circumstances it is conceivable that the primary particles might come out of the nucleus with energies varying over a considerable range and thus constitute a continuous spectrum. Since it now appears fairly certain that the disintegration takes place *first*, we expect the primary particles to be emitted with sharply quantised energy. They should then of course appear as a line in the β-ray spectrum. In the case of RaD, conditions are particularly simple. It emits only one γ-ray. Therefore we should anticipate that the number of primary β-particles would be equal to the number of γ-rays emitted. If this were true the primary line would be the strongest line, since the energy of the γ-ray has been shared among

the various atomic levels. This argument would rule out the line $H\rho = 742$ as a primary β-ray line.

There are at least two ways to account for the absence of the primary β-ray line. One possibility is a suggestion due to Rosseland.[7] He proposed the explanation that the particles originally leave the nucleus with a definite energy. In passing through the strong fields in the neighborhood of the nucleus they might be expected to radiate energy. He calculated this possible loss of energy by radiation and found that it was of the right order of magnitude to distribute the particles into a continuous spectrum. This explanation requires that variable portions of the energy be radiated and it is hard to see why this should happen. Much more information is needed concerning the intensity of the continuous spectrum before this question can be answered. Another possibility, though a somewhat doubtful one, enables us to eliminate both the continuous spectrum and the primary line from the β-ray spectrum. If we adopt Meitner's view and assume that the primary particle has energy exactly equal to that of the γ-ray, we may suppose that this primary particle experiences an inelastic collision with the first electron in the atomic levels which has less binding energy than that of the primary particle. The result would be a binding of the β-particle in the atomic level and the ejection of the electron originally in the level. However, this ejected electron should have exactly the same energy as those expelled by the γ-radiation. Therefore they would form part of the same line on the photographic plate. Presumably this could take place at other levels of lower energy so that most or all of the primary particles were absorbed. Therefore we should have little or no primary β-radiation and no continuous spectrum. The great difficulty with this hypothesis is that such collisions from any ordinary point of view must be relatively improbable. However, to explain the intensity of the lines, considering all γ-radiation to be converted in the atomic levels of the atom from which it originates, we are forced to assume an abnormally high coefficient of absorption for the γ-ray. It may well be that the same is true for a β-particle travelling from the nucleus out through the various electron levels. Since there is considerable radiation from neighboring atoms present, some support for this view can also be obtained from Milne's[8] statistical analysis of the liberation of photo-electrons. He finds that he is compelled to assume that external radiation can stimulate the capture of an electron. This might make it possible to account for the high probability of capture necessary on this view.

In conclusion, I should like to thank Dr. S. C. Lind of the Fixed Nitrogen Laboratory, for providing me with the old radon tubes from

[7] Rosseland, Zeits. f. Physik **14**, 173 (1923).

which the RaD sources were obtained, and Dr. Bardwell for much valuable advice concerning the manipulation of this material.

Note added to proof: Since the above paper was submitted for publication the library has received the issue of the Proceedings of the Cambridge Philosophical Society for November, 1925. A series of remarkable papers in this number present evidence indicating that the gamma-ray follows the disintegration for RaB and RaC. Rutherford and Wooster (Proc. Camb. Phil. Soc. **22**, 832, 1925) show that RaB emits the natural L spectrum of atomic number 83. Of course this is not a conclusive proof of the emission of the gamma-ray after disintegration. There is a possibility that the gamma-ray is emitted before disintegration but that the *x-ray transitions* are delayed and occur after the disintegration. The significant point of their result is that it does not contradict the supposition that the disintegration occurs first. If, on the other hand, the x-ray spectrum of atomic number 82 had been obtained there could be no doubt that the disintegration followed the gamma-ray emission. In confirmation of the results obtained by Rutherford and Wooster, Black has measured some of the lines of the natural L beta-ray spectrum of RaB. He also finds that these correspond to atomic number 83. Since this phenomenon is one step further removed from the emission of the gamma-ray than the one investigated by Rutherford and Wooster, it likewise does not constitute a *proof* that the gamma-ray follows disintegration. However, Ellis and Wooster (Proc. Camb. Phil. Soc. **22**, 844, 1925) have devised an experiment which seems to give definite proof. They wrapped a radon tube in platinum foil and then exposed the platinum surface in radon and obtained the active deposit on the outside of the platinum wrapping. Using this as a source in a beta-ray spectrograph they obtain the natural beta-ray spectra of RaB and RaC from the active deposit and the similar spectra excited in the platinum foil by the gamma radiation from the radon. They thus obtain a $\delta H\rho$ for each of the observed lines corresponding to the difference between the K, L, etc., energy for platinum and for RaB and RaC. This enables them to determine whether these levels are those of 82, 83 or 84. The measurements given in their paper very decidedly favor atomic number 83 for the lines of the RaB spectrum and atomic number 84 for the lines of the RaC spectrum. These results are thus a confirmation of the hypothesis proposed by Meitner that the disintegration *precedes* the emission of the gamma-ray, and there now seem to be no exceptions to this rule.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
December 15, 1925.

[8] E. A. Milne, Phil. Mag. **47**, 222 (1924).

THE ABSORPTION OF X-RAYS OF WAVE-LENGTH DOWN TO .08A

By S. J. M. Allen

Abstract

Mass absorption coffiecients of C, paraffine, S and 16 metal elements from Al to U for wave-lengths .56 to .08A have been measured in continuation of previous work[1] which covered most of these elements in the range .71 to .10A. The general radiation from a tungsten target (operated at voltages up to 200 kv) was dispersed by a crystal into an ionization chamber. By using Soller multiple slit collimators about ten times as great intensity was obtained as with a single slit of the same resolving power. The main results of the previous paper were confirmed and extended, especially the steady decrease in the "jump" of the absorption in going from the L to the K regions, as the atomic number increases. The scattering of paraffine wax is distinctly greater than that of C or Al, probably due to the richness of H in paraffine. The empirical formula $\mu/\rho = C\lambda^{2.92}N^4/A + \sigma/\rho$, applied to the experimental results gives values of σ/ρ which increase in general with atomic number, becoming about 1 for the heavier elements, W to Bi. The values of C obtained are .0132 for the K series and .00181 for the L series; these give calculated values which agree within 5 percent with the experimental. *Experiments with end-filtered high voltage rays.* Without collimators or crystal, the ionization chamber in the path of the direct beam of rays filtered through 1 cm tin and 2 cm aluminum, showed increased ionization when a carbon block was interposed, but when two Soller collimators were used with planes crossed so as to eliminate all oblique rays, normal absorption coefficients were obtained corresponding to .075A. This method may be useful for the shortest rays.

IN a previous paper[1] the author gave results of experiments on the absorption of homogeneous x-rays from $\lambda = .71$ to .10A following the standard method of reflecting the general radiation of a Coolidge tube from a crystal, and intercepting a narrow portion of the spectrum with an ionization chamber attached to the spectrometer.

It was shown that as the wave-length approached .10A, the K absorption coefficients of the high weight elements were decreasing steadily according to the laws of fluorescent absorption, but that in the case of the light elements fluorescent absorption being practically gone, further decrease was very slow. Also, that in the critical absorption regions of the elements the "jump" of the absorption coefficients from the L series to the K series became steadily less with increasing atomic number. This was especially marked in the case of the elements from W to Bi, with

[1] Allen, Phys. Rev. **24**, 1 (July 1924).

the result that the K absorption coefficients of these elements were nearly the same.

It was further shown that the Bragg-Owens' empirical absorption law, $\mu/\rho = C\lambda^3 N^4/A + \sigma/\mu$ was no longer able to predict values of μ/ρ for the high weight elements which agreed with the experimental values obtained. In all the discussion which follows in this paper μ/ρ will represent the experimentally determined mass absorption coefficient, τ/ρ the fluorescent absorption coefficient of the electronic orbits, (K, L, M, etc.), and σ/ρ the remainder of the absorbed energy, which may or may not be entirely due to pure scattering.

The present paper is a continuation of the above work, and carries the wave-length down to .08A. While these experiments were carried out in the same general manner as the former ones, the technique of operation was so different as to necessitate a brief description.

The source of the rays, up to a potential of 120 kv was a Coolidge Universal tube,and up to 200 kv a Coolidge high tension tube. The tube, generator, and all high tension connections were placed by themselves in a closed room, completely shut off from the adjacent room, where the spectrometer was placed, by a brick wall two feet thick and lined with lead. A hole was pierced through the wall and two lead slits 1 cm square placed at each end, defined the beam of rays from the tube.

In place of the usual single slit method, the multiple slit collimators, devised in my laboratory by Soller[1] were employed. The first collimator was placed directly in front of the crystal with its axis passing through the axis of rotation of the spectrometer and perpendicular to it. The second collimator was attached to the ionization chamber, and in the zero position its axis was coincident with that of the first. Each collimator was 8 cms long, 1 cm wide, 1 cm high and had slits about .2 mm wide.

The general radiation passing through the first collimator emerged as a number of thin beams parallel to each other in a vertical plane. This beam falling upon a calcite crystal 2 cms thick passed through it, the reflected radiation being obtained from the interior 100 planes. The zero position having been determined, the ionization chamber was swung around to some angle 2θ. The crystal was now rocked back and forth until maximum radiation was received, when it was assumed that radiation of wave-lengths between λ and $\lambda + d\lambda$ alone passed through the second collimator. The mean wave-length λ was calculated from the relation, $\lambda = 2d \sin \theta$.

[1] Soller, Phys. Rev. **24**, 158 (1924).

The resolving power was quite equal to that obtained with single slits of .1 to .2 mm.

It was found that this method gave about ten times the intensity that could be obtained with single slits at the same resolving power. Another great advantage of this method lies in the fact that the zero position once having been obtained does not change with penetration of the rays into the crystal, δ being obtained solely from 2θ the angle between the axes of the two collimators.

The rest of the experiment was carried out in the usual manner, the absorbing layers being placed on the side of the wall next to the tube, thus ensuring that no scattered radiation from these layers could enter the ionization chamber.

Although rays reflected from the crystal at values of θ less than that corresponding to $\lambda = .081$A were observed, difficulties of resolution were encountered which rendered them somewhat uncertain, and so results are here given only down to $\lambda = .081$A. It is hoped that a redesign of

TABLE IA

Mass absorption coefficients μ/ρ

λ in A	C	Paraffine	Al	S	Fe	Ni	Cu	Zn	Pd
.081	.143	.156	.145	.155	.235	.265	.270	.310	.73
.085	.145	.158	.153	.170	.242	—	.280	—	.80
.090	.148	.160	.160	.182	.250	.290	.295	.350	.86
.095	.150	.165	.164	.186	.262	—	.305	—	—
.102	.150	.171	.169	.192	.280	.337	.335	.390	1.11
.113	—	—	—	—	.317	—	.405	—	—
.118	.151	.175	.172	.196	.360	—	.440	.520	—
.126	—	—	—	—	.410	.480	.510	—	—
.135	—	—	—	—	.460	—	.600	.690	—
.140	.152	.180	.195	.250	.500	—	.650	—	—
.145	—	—	—	—	.540	—	.710	.820	—
.148	—	—	—	—	—	—	—	—	—
.151	.153	—	—	—	.595	.690	.780	—	—
.160	—	.185	.212	.295	.660	—	.900	1.02	—
.164	—	—	—	—	—	—	—	—	—
.173	.155	.190	.235	.330	.780	1.00	1.09	1.24	—
.185	—	—	.249	.360	.90	1.18	1.30	1.47	—
.194	—	—	.265	—	1.00	—	—	—	—
.209	.166	.196	.295	.440	1.26	1.63	1.71	2.01	—
.220	—	—	.310	.500	1.40	—	2.00	2.32	—
.240	.170	.200	.356	.580	1.75	2.28	2.50	2.80	—
*.280	—	—	.475	.800	2.75	3.38	3.70	4.30	—
*.320	.200	.220	.630	1.08	3.95	4.87	5.25	6.20	—
*.340	—	—	.730	1.23	4.65	5.75	6.38	7.30	—
*.400	.245	.245	1.11	1.78	7.25	—	8.80	11.6	—
.430	—	—	1.33	2.10	—	—	12.5	14.5	—
.458	.288	—	1.54	—	—	—	14.7	17.2	—
.511	—	.34	2.06	—	—	—	20.5	24.0	—
.560	.40	.36	2.65	—	—	—	26.5	30.8	—
*.631	.55	—	3.78	6.9	—	—	37.8	43.0	—
*.710	.68	—	5.35	9.9	—	—	53.7	60.0	—

* Taken from previous paper.

the apparatus will in the future enable me to obtain results for shorter wave-lengths.

In Tables IA and IB are tabulated results of this work, and also a number of the results of the preceding work, which are indicated by asterisks. The vertical double arrows indicate the regions of critical

TABLE IB

Mass absorption coefficients μ/ρ

λ in A	Ag	Sn	Ba	W	Pt	Au	Pb	Bi	Th	U
.081	.74	.80	—	2.40	2.50	2.44	2.53	2.50	—	—
.085	.83	.88	—	2.60	2.75	2.65	2.78	2.76	—	—
.090	.90	.95	—	2.80	2.95	2.85	3.00	3.00	—	—
.095	1.02	1.02	—	3.10	3.38	3.30	3.45	3.45	—	3.53
.102	1.17	1.20	—	3.50	3.80	3.76	3.90	3.90	4.00	↕
.113	—	1.52	—	4.30	4.50	4.48	4.70	4.70	↕	1.78
.118	1.57	1.77	1.95	4.75	5.00	4.90	5.13	4.90	↕	—
.126	1.68	2.05	—	5.35	5.70	5.50	5.23	↕	1.86	1.90
.135	—	2.40	—	6.25	6.55	6.40	↕	↕	2.10	—
.140	2.40	2.62	2.80	6.75	7.08	6.90	↕	↕	2.25	2.56
.145	—	2.90	—	7.30	7.55	7.40	↕	2.25	2.48	—
.148	—	—	—	7.75	7.70	↕	↕	—	—	—
.151	2.65	3.15	3.40	8.00	↕	↕	2.45	2.48	2.72	3.78
.160	—	3.60	4.00	8.90	↕	↕	2.70	2.90	3.10	—
.164	—	—	—	↕	↕	2.70	—	—	—	3.24
.173	3.75	4.32	4.90	↕	2.90	3.02	3.25	3.50	3.75	—
.185	4.40	5.05	5.80	↕	3.48	3.55	3.85	4.14	4.45	—
.194	5.00	—	7.0	3.20	3.90	—	4.40	—	5.05	—
.209	6.50	6.95	8.2	3.93	4.70	4.87	5.35	5.60	6.10	—
.220	7.40	8.30	9.2	4.20	5.25	5.50	5.90	6.48	6.90	—
.240	9.60	10.80	11.7	5.10	6.65	6.95	7.40	8.30	8.60	—
*.280	14.8	15.5	17.2	7.20	9.60	—	11.5	12.5	—	—
*.320	21.1	22.0	24.2	10.1	13.5	—	16.2	17.7	—	—
*.340	24.5	—	6.0	12.0	15.8	—	19.7	21.0	—	—
*.400	38.2	—	9.0	19.8	24.5	—	31.8	—	—	—
		↕								
.430	46.5	8.0	11.5	24.7	30.0	—	39.0	—	—	—
.458	60.0	9.0	13.7	29.7	35.5	—	46.0	—	—	—
	↕									
.511	10.0	12.8	19.0	—	—	—	—	—	—	—
.560	15.0	16.5	—	—	—	—	—	—	—	—
*.631	20.5	—	—	75	87	—	101	—	—	—
*.710	28.5	—	—	—	119	—	140	—	—	—

* Taken from previous paper.

absorption, the upper limit being the highest K values, and the lower the lowest L values. In the cases of Ba, Th, and U, the values given are the values which probably would have been obtained if these substances had been in the pure state. They were calculated assuming the additive law. Paraffine was in the form of paraffine wax.

Table II gives the values of the critical absorption wave-lengths as obtained from the data of Tables IA and IB. These values agree in general to within one percent with those published by other observers.

A detailed study of the absorption coefficients of Tables IA and IB shows that they are of the same character as those of the preceding work. The "jumps" in the values of τ/ρ from L series to K series steadily decrease with increasing atomic number, that for U being about 4. The K absorption coefficients from W to U are nearly all the same, for the

TABLE II

Critical absorption wave-lengths λ_c

Element:	U	Th	Bi	Pb	Au	Pt	W	Ba	Ag
λ_c in A:	.105	.113	.132	.139	.154	.159	.178	.330	.484

same wave-lengths, and it would require an accuracy of one percent or better to decide whether there is any real difference. The decrease in μ/ρ with λ is about the same for all. The intermediate elements, such as Ag, Sn and Ba, show values of σ/ρ which decrease much more slowly with λ, indicating that σ/ρ which decreases slowly is becoming of increasing importance in comparison with τ/ρ. The values of μ/ρ for the light elements as $\lambda = .08$A is approached show such small rates of change, that for these elements τ/ρ is fast disappearing as an important factor, and σ/ρ is now the predominating factor. In the case of C the change in μ/ρ from $\lambda = .160$ to $\lambda = .081$A is only a few percent, and even this small rate of decrease is becoming smaller as we approach .08A. The same is true of paraffine, Al and S. μ/ρ for paraffine wax at $\lambda = .081$A is distinctly greater than that of C or Al, whilst at $\lambda = .40$A it is equal to that of C and much less than that of Al. This can be probably explained by assuming that σ/ρ for H is greater than that for C, for since paraffine wax is rich in H, it will show correspondingly larger values of σ/ρ and smaller values of τ/ρ than C.

The same phenomenon has been found for substances rich in H by other observers at longer wave-lengths.

There is no evidence that σ/ρ is experiencing any sudden or rapid decrease with λ.

If we are justified in concluding from the above results that the true mass scattering coefficient for light elements will continue to decrease at such a slow rate it is difficult to see how it can arrive for $\lambda = .02$A at such a low value for C as .056 for the filtered γ rays of radium C, which the recent work of Ahmad,[2] Ahmad and Stoner,[3] and that of Owen, Fleming and Fage[4] would seem to indicate. It is possible that there estimations of λ are much too high.

[2] Ahmad, Proc. Roy. Soc. **A105,** 507 (1924).
[3] Ahmad and Stoner, Proc. Roy. Soc. **A106,** 8 (1924).
[4] Owen, Fleming and Fage, Phys. Soc. Proc. **36,** 355 (August, 1924).

In Table III are expressed some estimated values of, σ/ρ, calculated from the data of Tables IA and IB by aid of the formula, $\sigma/\rho=\mu/\rho-k\lambda^{2.92}$. If this formula holds for these short wave-lengths for both the K series (excluding elements W to U) and the L series, the results indicate that σ/ρ increases with N, reaching in the L series of the heavy elements values possibly as high as 1.0. Similar results are obtained if we use λ^3, only they are larger.

TABLE III

Mass scattering coefficients, $\sigma/\rho=\mu/\rho-k\lambda^{2.92}$

Element	λ.08A	λ.120A	λ.210A	λ.320A	λ.440A
		K series			
Carbon	.142	.148	.151	.148	.145
Paraffine	.155	.155	.184	.180	.169
Aluminum	.136	.144	.150	.130	.140
Sulfur	.138	.144	.170	.150	—
Iron	.165	.160	.200	.21	.25
Copper	.175	.160	.24	.03	—
Zinc	.195	—	—	—	—
Silver	.370	.43	.50	.3	—
Tin	.380	.45	—	—	—
Barium	—	.51	.70	—	—
		L series			
Tungsten, Platinum, Gold, Lead, Bismuth	.9 to 1.0	.75 to 1.1	1.0 to 1.2 to 1.1 to 1.0	—	—

Now, if σ/ρ, which here merely means the rest of the energy lost after fluorescent absorption has been allowed for, is completely due to pure scattering, then it should decrease in general with increase of N, being proportional to N/A in any of the theoretical formulas of, Thomson, Compton, or Jauncey.

It is evident that either one cannot use these empirical formulas to predict the values of τ/ρ at these short wave-lengths, or, if one can, then the values of σ/ρ so obtained are much larger in many cases than the theoretical formulas of pure scattering would indicate.

It is also possible that the experimental values of σ/ρ are not wholly due to pure scattering, but may involve some form of absorption, either true absorption, or scattering, or both, not associated with the K, L, etc. orbits, such as perhaps nuclear absorption.

It is important to call attention to the fact that Barkla and his associates in several papers on relative scattering state that the relative scattering of heavy elements to light elements increases rapidly with N, and also with λ.

Also Debye[5] from theoretical considerations predicts, that in the case of scattering from atoms where the electrons are not free but concentrated near the center, the atomic scattering coefficient would be proportional to a higher power of N than the first, in the limiting case (electrons at the center) being proportional to N^2. For mass scattering this would give σ/ρ proportional to $N^2/2$ instead of N/A.

Until one has obtained by a direct method true values of σ/ρ, it may not seem very fruitful to try to distinguish, in the region of short wave-lengths, between the various empirical absorption formulas. The generally accepted one is

$$\left.\begin{aligned} \mu/\rho &= C\lambda^3 N^4/A + \sigma/\rho \ldots\ldots\ldots\ldots \text{(mass)} \\ \mu_a &= C_a\lambda^3 N^4 + \sigma_a \ldots\ldots\ldots\ldots\ldots \text{(atomic)} \end{aligned}\right\} (1).$$

The author has proposed the following—

$$\left.\begin{aligned} \mu/\rho &= C\lambda^{2.92} N^4/A + \sigma/\rho \ldots\ldots\ldots\ldots \text{(mass)} \\ \mu_a &= C_a\lambda^{2.92} N^4 + \sigma_a \ldots\ldots\ldots\ldots\ldots \text{(atomic)} \end{aligned}\right\} (2)$$

Within the limits in which these formulas may be used to predict results to about five percent, I have, from the data of these two papers, and from those given by Bragg and Pierce,[6] Hewlett,[7] Richtmyer,[8] Windgarth,[9] and Stoner and Martin,[10] calculated the best values of C and C_a. These are expressed in Table IV.

TABLE IV

Values of C and C_a

	K series		L series	
	Eqs. (1)	Eqs. (2)	Eqs. (1)	Eqs. (2)
C	1.36×10^{-2}	1.32×10^{-2}	1.86×10^{-3}	1.81×10^{-3}
C_a	2.24×10^{-26}	2.19×10^{-26}	3.06×10^{-27}	3.00×10^{-27}

The experimental data of Tables 1A and IB discussed above are also illustrated by the graphs of Figs. 1, 2, 3, and 4. Figs. 1 and 2 show the relations between μ/ρ and $\lambda^{2.92}$. Figs. 3 and 4 show the relations between μ/ρ and N^4/A. Values of J from the graphs of 1 and 2 are tabulated. Also values of C_K and C_L are tabulated from Figs. 3 and 4.

In order to ascertain what reliance could be placed upon "end" filtered rays at high voltage, the following experiments were made at 200 kv.

[5] Debye, Ann. d. Physik **46,** 809 (1915).
[6] Bragg and Pierce, Phil. Mag. **8,** 608 (1914).
[7] Hewlett, Phys. Rev. **17,** 284 (1921).
[8] Richtmyer, Phys. Rev. **18,** 13 (1921).
[9] Windgarth, Car Bloms Boktrycheri, Lund (1923).
[10] Stoner and Martin, Proc. Roy. Soc. **A107,** 1925.

The two collimators being removed temporarily, and the ionization chamber turned to the zero position, a filter of 1 cm tin and 2 cms alu-

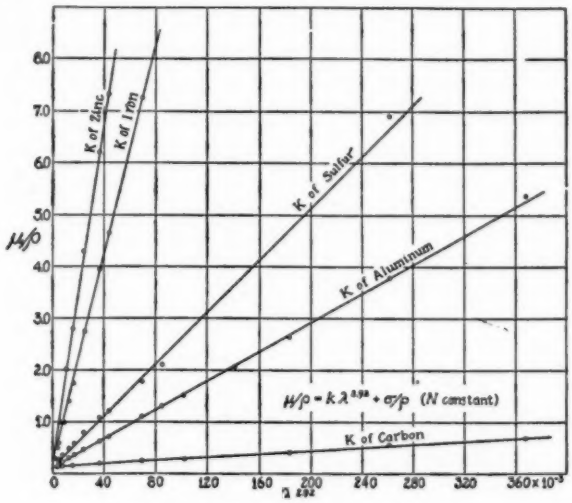

Fig. 1. Variation of μ/ρ with $\lambda^{2.92}$.

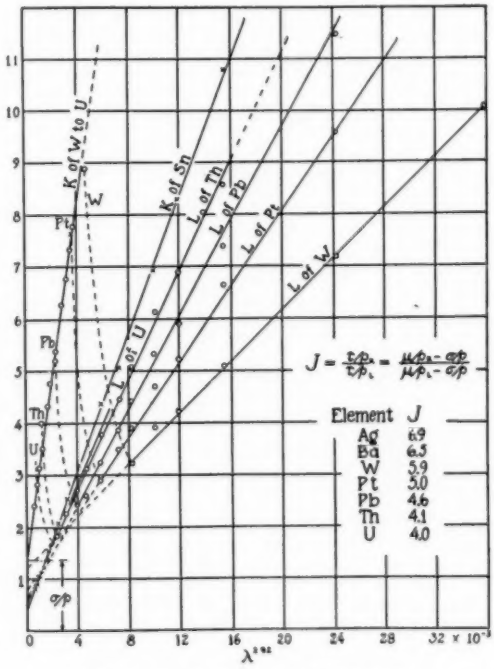

Fig. 2. Variation of μ/ρ with $\lambda^{2.92}$.

minum was placed next to the tube. A reading of the electroscope was then taken in arbitrary units, say 100. A block of carbon was then

placed directly behind the filter to intercept the rays before they passed through the wall. The somewhat surprising result was now obtained that the ionization was increased to 300 instead of being decreased.

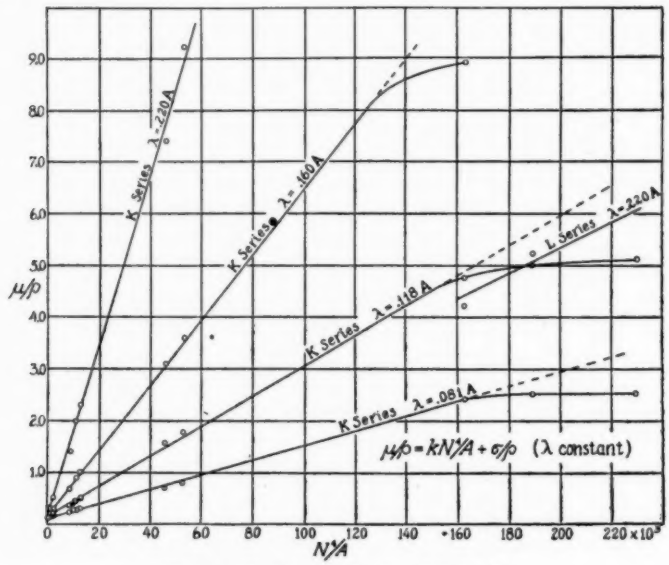

Fig. 3. Variation of μ/ρ with N^4/A.

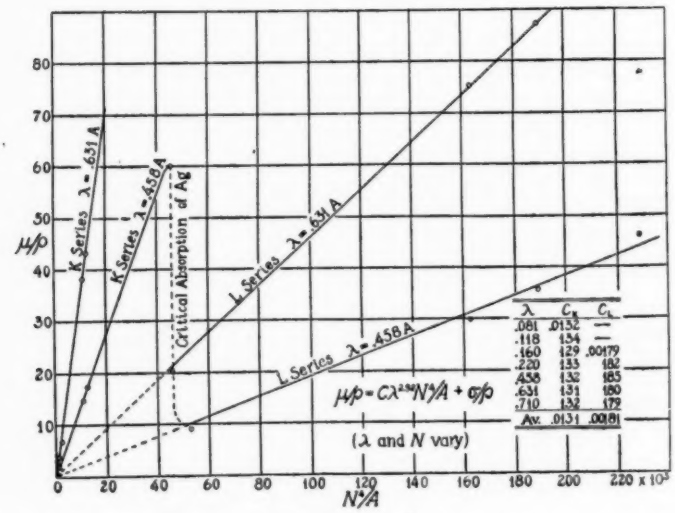

Fig. 4. Variation of μ/ρ with N^4/A.

The same result was obtained with other elements, but in a lesser degree for the heavier elements. It is thus seen that more rays were scattered

in the direction of the direct beam, than were scattered away. Under these conditions absorption coefficients would have no true significance.

Next the collimators were placed in position, with axes coincident but with their planes crossed at right angles. Readings taken now, show normal results, and it makes no difference where the absorbing layer is placed. Only those rays which pass straight forward can enter the ionization chambers, all oblique rays in both horizontal and vertical directions being eliminated.

In Table V are given the results of this last experiment. The effective wave-length viz. $\lambda = .075$A was calculated from μ/ρ for Ag and Sn. The values in this table are in good conformity with those obtained by the crystal method at $\lambda = .08$A.

TABLE V

X-rays filtered through Sn, voltage 200,000, $\lambda_{eff.} = .075$ A

Element:	C	Par.	Al	S	Fe	Ni	Cu	Zn	Ag	Sn	Pt	Au	Pb	Bi
μ/ρ	.140	.145	.147	.155	.22	.24	.25	.28	.69	.72	2.02	2.12	2.33	2.42

Since at these high voltages the energy of the spectrum is largely concentrated in the short wave-lengths, "end" filtering with crossed collimators will give results of some importance, when one is no longer able to obtain homogeneous rays from crystal reflection, at least in those elements which are far removed from their critical absorption regions.

Absorption coefficients obtained in the past from filtered "end" rays which have seemed to indicate very small values of μ/ρ at high voltages are of doubtful value, unless precautions similar in effect to those discussed above were taken.

In conclusion it may be of advantage briefly to review the chief points brought out by the experimental results of these two papers.

A careful analysis of the absorption coefficients of the elements from C to U for values of λ between .71 and .08A, shows quite clearly that no general formula of absorption of the Bragg-Owens type can predict values which agree with experimental ones in both the L and K series by simply changing the constant. In the L series it will predict values increasingly too low, and in the K series increasingly too high, as we proceed to the high atomic weight elements. The experimental fact, that the decreasing jumps in the absorption coefficients from the L series to the K series, which results in the coefficients of the elements from W to U being nearly the same for the same wave-lengths, will explain the failure in the case of the K series.

In the case of the L series, the difference σ/ρ between the experimental value of μ/ρ and the calculated value of τ/ρ is too great to be entirely

accounted for by pure scattering according to the theories of Thomson, Compton, and Jauncey. It therefore seems necessary to raise the question whether in addition to fluorescent absorption and pure scattering there may exist nuclear absorption of some kind, which in the case of high weight atoms is great enough to be experimentally distinguished.

In the case of light atoms where fluorescent absorption has practically disappeared, the experimental results show that the absorption is decreasing with λ at a very slow rate.

Until one is able to determine in a region of wave-lengths where τ/ρ is very large in comparison with σ/ρ, the exact variation of τ/ρ with λ, the method of this paper in estimating σ/ρ may be open to some question. The author is at present engaged in measuring the absorption coefficients of wave-lengths greater than 1A and it is hoped that the results of this investigation in the near future may throw more light on the problem.

UNIVERSITY OF CINCINNATI,
November 3, 1925.

REFLECTION OF RADIATION FROM A FINITE NUMBER OF EQUALLY SPACED PARALLEL PLANES

By T. H. Gronwall

Abstract

Equations are derived for the fractions of the incident energy which are absorbed, reflected and transmitted by $n+1$ equally spaced parallel planes, taking account of all possible internal reflections, in terms of the corresponding fractions for a single plane, a, r and t respectively. When a and r are very small, as in the case of x-rays incident on a crystal surface, they may be computed from measurements of the reflected fraction R_N for N large, and of the transmitted fraction T_n, for n small.

1. *Introduction.* In dealing with the reflection, transmission and absorption of radiation in a crystalline medium, we assume the molecules of the medium to be situated in a number of equally spaced parallel planes (and to have the familiar lattice arrangement). We assume that when a ray of intensity I strikes one of these planes, a part of it, which we denote by rI, is reflected, another part tI transmitted, and the remaining part aI absorbed, so that

$$r+t+a=1. \tag{1}$$

These constants r, t and a are assumed to be the same for all planes.

Let us consider $n+1$ of these planes, numbered 1, 2, . . . , n, $n+1$, and a ray of intensity I striking the first plane; taking into account all possible modes of reflection at one or more of the planes, a certain part T_nI will be transmitted across the $n+1$ plane, another part R_nI will be reflected, that is, will emerge on the same side of the first plane as the incident ray I, and the remaining part A_nI is absorbed by the $n+1$ planes; we evidently have

$$R_n+T_n+A_n=1. \tag{2}$$

Our problem is to express R_n and T_n (and hence, by (2), also A_n) in terms of r, t and n, and it is obviously permissible to assume $I=1$ in the following discussion.

2. *Determination of R_n and T_n for $n=0$ and $n=1$.* In the case of a single plane ($n=0$) it follows at once from the definitions that

$$R_0=r, \qquad T_0=t. \tag{3}$$

In the case of two planes, numbered 1 and 2, a ray of unit intensity striking plane 1 gives a reflected ray r and a ray t penetrating plane 1, and when the latter ray strikes plane 2, it gives a transmitted ray $t \cdot t = t^2$ and a ray tr reflected from plane 2 toward plane 1. At the latter plane, this tr gives a ray $t \cdot tr = t^2 r$ penetrating the plane toward the side of the incident ray, so that $t^2 r$ is a component of the total reflected ray R_1, while a ray $r \cdot tr = tr^2$ is reflected toward plane 2. This tr^2 penetrates plane 2 in the amount $t \cdot tr^2 = t^2 r^2$, which forms a component of the total transmitted ray T_1, while a ray $r \cdot tr^2 = tr^3$ is reflected toward plane 1, giving at the latter a component $t \cdot tr^3 = t^2 r^3$ of R_1 and a ray $r \cdot tr^3 = tr^4$ reflected toward plane 2, where it gives a component of T_1 equal to $t \cdot tr^4 = t^2 r^4$ and a ray $r \cdot tr^4 = tr^5$ reflected toward plane 1. Continuing in this manner, we find for the sums of the components of the transmitted and reflected rays the expressions

$$T_1 = t^2 + t^2 r^2 + t^2 r^4 + \cdots ,$$
$$R_1 = r + t^2 r + t^2 r^3 + t^2 r^5 + \cdots ,$$

or summing the geometric series to the right

$$T_1 = t^2/(1-r^2) , \qquad R_1 = r + t^2 r/(1-r^2) . \tag{4}$$

3. *The two difference equations for R_n and T_n.* Proceeding to the general case, our first step consists in setting up two difference equations (that is, recurrent formulas) connecting T_{n+1} and R_{n+1} with T_n and R_n. Consider the $n+2$ planes numbered $1, 2, \ldots, n+1, n+2$; these we divide in two layers, the first layer consisting of the planes numbered $1, 2, \ldots, n+1$, and the second of those numbered $n+1$ and $n+2$. The plane numbered $n+1$, common to both layers, is called the boundary plane between them. It will be convenient to separate the reflected ray R_n in the ray r reflected directly at plane 1 and the remainder R'_n reflected at other planes after penetrating into the layer, so that

$$R_n = r + R_n' , \qquad R_{n+1} = r + R'_{n+1} , \tag{5}$$

and (3) and (4) show that

$$R_0' = 0 , \qquad R_1' = t^2 r/(1-r^2) . \tag{6}$$

Now consider a ray of unit intensity striking the first layer at plane 1; the ray T_{n+1} transmitted through both layers is made up of components which we classify according to the number of times they cross the boundary plane between the first layer and the second. The component crossing the boundary plane once is obtained thus: let t_n' be a ray which is transmitted into the second layer after a certain number of trans-

missions and reflections in the planes of the first layer. Since the intensity of a transmitted ray is multiplied by t in the passage through a plane, it follows that the intensity of t_n' immediately before passing through the boundary plane is $t_n' \cdot t^{-1}$. Passing through the second layer, which consists of two planes, the intensity becomes $t_n' t^{-1} \cdot T_1$, and our component is the sum of $t_n' t^{-1} \cdot T_1$ extended over all partial rays t'_n; the sum of the latter being T_n, the component of T_{n+1} arising from all partial rays crossing the boundary plane once is $T_n t^{-1} \cdot T_1$. Any ray transmitted through both layers must evidently cross the boundary plane an odd number of times. Hence the next component of T_{n+1} crosses the boundary plane three times and is obtained by taking the component $T_n t^{-1}$ arriving at the boundary plane and multiplying it by $R_1' t^{-1}$, thus forming a component which has crossed the boundary plane and been reflected in the interior of the second layer, but has not yet crossed the boundary plane the second time. Observe that we multiply by $R_1' t^{-1}$ and not by $R_1 t^{-1} = (r + R_1') t^{-1}$, since we are not concerned with those rays that are reflected at the boundary plane without penetrating into the second layer. This component $T_n t^{-1} \cdot R_1' t^{-1}$ we multiply by $R_n' t^{-1}$, thus obtaining a component which has crossed the boundary plane twice and been reflected in the interior of the first layer, but has not yet crossed the boundary plane for the third time. The third crossing of the boundary plane and transmission through the second layer multiplies our component by T_1, so that the component of T_{n+1} resulting from crossing the boundary plane three times will be

$$T_n t^{-1} \cdot R_1' t^{-1} \cdot R_n' t^{-1} \cdot T_1 ,$$

where each multiplication point stands at a crossing of the boundary plane. Similarly, the component which crosses the boundary plane five times is

$$T_n t^{-1} \cdot R_1' t^{-1} \cdot R_n' t^{-1} \cdot R_1' t^{-1} \cdot R_n' t^{-1} \cdot T_1 ,$$

and so on. Finally T_{n+1} is the sum of all these components, so that

$$T_{n+1} = T_n t^{-1} T_1 [1 + R_1' R_n' t^{-2} + (R_1' R_n' t^{-2})^2 + \cdots] ,$$

or by (4) and (6)

$$T_{n+1} = \frac{t T_n}{1 - r^2} \left[1 + \frac{r R_n'}{1 - r^2} + \left(\frac{r R_n'}{1 - r^2} \right)^2 + \cdots \right].$$

The geometric series to the right converges, since $R_n < 1$ by (2), so that $R_n' < 1 - r$ by (5) and $r R_n'/(1 - r^2) < r/(1 + r) < 1$; summing the series, we obtain

$$T_{n+1}=\frac{t}{1-r^2}\cdot\frac{T_n}{1-\dfrac{r}{1-r^2}R_n'}\,. \tag{7}$$

Turning our attention to the reflected ray R_{n+1} and reasoning in exactly the same manner, we have first the component R_n which does not cross the boundary plane, then the component crossing the boundary plane twice which is $T_nt^{-1}\cdot R_1't^{-1}\cdot T_n$, next the component $T_nt^{-1}\cdot R_1't^{-1}\cdot R_n't^{-1}\cdot R_1't^{-1}\cdot T_n$ crossing the boundary plane four times, and so on, their sum being

$$R_{n+1}=R_n+T_n^2R_1't^{-2}[1+R_1'R_n't^{-2}+(R_1'R_n't^{-2})^2+\cdots]\,,$$

whence, replacing R_n and R_{n+1} by $r+R_n'$ and $r+R_{n+1}'$ according to (6) and observing that the series to the right is the same as in the expression for T_{n+1},

$$R'_{n+1}=R_n'+\frac{r}{1-r^2}\cdot\frac{T_n^2}{1-\dfrac{r}{1-r^2}R_n'}\,. \tag{8}$$

Equations (7) and (8) are the desired difference equations.

4. *Solution of the difference equations for R_n and T_n.* We now introduce the notation

$$\rho_n=1-\frac{r}{1-r^2}R_n'\,, \tag{9}$$

whence, by (6),

$$\rho_0=1\,,\qquad \rho_1=1-\frac{t^2r^2}{(1-r^2)^2}\,; \tag{10}$$

since $0<R_n'<1-r$, it follows from (9) that

$$\frac{1}{1+r}<\rho_n<1\,. \tag{11}$$

Introducing ρ_n in Eqs. (7) and (8), these take the form

$$T_{n+1}=\frac{t}{1-r^2}\cdot\frac{T_n}{\rho_n}\,, \tag{12}$$

$$\rho_n-\rho_{n+1}=\frac{r^2}{(1-r^2)^2}\cdot\frac{T_n^2}{\rho_n}\,, \tag{13}$$

From these, we form a difference equation of the second order for ρ_n by eliminating T_n in the following manner: in (13), replace n by $n+1$ and in the result, substitute the value of T_{n+1} from (12), whence

$$\rho_{n+1}-\rho_{n+2}=\frac{r^2}{(1-r^2)^2}\cdot\frac{T^2{}_{n+1}}{\rho_{n+1}}=\frac{t^2r^2}{(1-r^2)^4}\cdot\frac{T_n{}^2}{\rho_{n+1}\rho_n{}^2}\,.$$

In the last expression, we substitute the value of $T_n{}^2$ taken from (13) obtaining

$$\rho_{n+1}-\rho_{n+2}=\frac{t^2}{(1-r^2)^2}\cdot\frac{\rho_n-\rho_{n+1}}{\rho_{n+1}\rho_n}=\frac{t^2}{(1-r^2)^2}\left(\frac{1}{\rho_{n+1}}-\frac{1}{\rho_n}\right).$$

Transposing terms, we obtain the difference equation of the second order

$$\rho_{n+2}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_{n+1}}=\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}\,, \tag{14}$$

which shows that the expression to the right remains unchanged in value when n is increased by unity. Starting with $n=0$, and increasing it by a unit at a time, it follows that the right hand member of (14) has the same value for any n as for $n=0$, so that

$$\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}=\rho_1+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_0}\,,$$

and calculating the expression to the right by means of (10), we find

$$\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}=1+\frac{t^2}{1-r^2}\,. \tag{15}$$

This difference equation of the first order is thus a first integral of (14), and is in its turn reduced to a directly integrable linear difference equation in the following manner. From (11) it is seen that ρ_n is positive, and from (13) that $\rho_n>\rho_{n+1}$. The sequence $\rho_0, \rho_1, \ldots, \rho_n, \ldots$ is thus decreasing toward a limit ρ:

$$\lim_{n\to\infty}\rho_n=\rho\,, \tag{16}$$

and (11) shows that

$$\frac{1}{1+r}\leqq\rho<1\,. \tag{17}$$

From (15) and (16) it is seen that ρ satisfies the equation

$$\rho+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho}=1+\frac{t^2}{1-r^2}\,, \tag{18}$$

and solving this quadratic in ρ,

$$2(1-r^2)\rho=1+t^2-r^2\pm\sqrt{(1+t^2-r^2)^2-4t^2}\,.$$

To determine the sign of the radical, we observe that $t<1-r$ by (1), so that (17) gives

$$>\frac{t}{1-r^2}\,; \tag{19}$$

on the other hand, the product of the roots of (18) equals $t^2/(1-r^2)^2$, and consequently (19) shows that the second root of (18) is less than $t/(1-r^2)$. Hence ρ is the greater of the two roots of (18) and corresponds to the plus sign before the radical. Resolving the expression under the radical sign into factors, we thus obtain

$$2(1-r^2)\rho=1+t^2-r^2+\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}\,. \tag{20}$$

As $n\to\infty$, R_n tends toward a limit R, which equals $r+(1-r^2)(1-\rho)/r$ by (5) and (9), so that, according to (20),

$$R=\frac{1}{2r}\left[1-t^2+r^2-\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}\,\right]. \tag{21}$$

An expression for this R, which is the reflection in an infinite number of equally spaced parallel planes, was found in an entirely different way by K. W. Lamson[1] in form of an infinite series, the sum of which was shown by the author to be (20).[2]

Returning to Eq. (15), we subtract from it Eq. (18), obtaining

$$\rho_{n+1}-\rho=\frac{t^2}{(1-r^2)^2}\left(\frac{1}{\rho}-\frac{1}{\rho_n}\right);$$

making the substitution

$$\rho_n=\rho\left(1+\frac{1}{\omega_n}\right), \tag{22}$$

the preceding equation becomes

$$\frac{\rho}{\omega_{n+1}}=\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho}\cdot\frac{1}{\omega_n+1},$$

and writing

$$\mu=\frac{1-r^2}{t}\rho, \tag{23}$$

[1] K. W. Lamson, Physical Review, N. S. **17**, 624 (1921), Eqs. (2) and (3).

[2] Lamson, l.c. Eq. (5). This formula contains two misprints: the minus sign between t^2 and r^2 should read plus, and a minus sign should be inserted between r^2 and the square root. For the proof, see T. H. Gronwall, Annals of Mathematics, ser. 2, **23**, 282 (1922).

so that $\mu>1$ by (19), this reduces to the linear difference equation in ω_n:

$$\omega_{n+1}=\mu^2(\omega_n+1)\ . \tag{24}$$

This may be written

$$\omega_{n+1}+\frac{\mu^2}{\mu^2-1}=\mu^2\left(\omega_n+\frac{\mu^2}{\mu^2-1}\right)\ ,$$

and this last equation is integrated immediately, giving

$$\omega_n+\frac{\mu^2}{\mu^2-1}=\mu^{2n}\left(\omega_0+\frac{\mu^2}{\mu^2-1}\right)\ .$$

Since $\rho_0=1$ by (10), we have $\omega_0=\rho/(1-\rho)$ by (22), so that finally

$$\omega_n+\frac{\mu^2}{\mu^2-1}=\left(\frac{\rho}{1-\rho}+\frac{\mu^2}{\mu^2-1}\right)\mu^{2n}. \tag{25}$$

Having thus determined ω_n explicitly as a function of r, t and n, we obtain R_n by the combination of (5), (9), and (22):

$$R_n=\frac{1}{r}-(1-r^2)\rho\left(1+\frac{1}{\omega_n}\right)\ . \tag{26}$$

For T_n, we find from (13) and (22)

$$\frac{r^2}{(1-r^2)^2}T_n^2=\rho^2\cdot\frac{1+\omega_n}{\omega_n}\cdot\frac{\omega_{n+1}-\omega_n}{\omega_n\omega_{n+1}}\ ,$$

or replacing ω_{n+1} by its expression from (24) and using (23),

$$T_n^2=\frac{t^2}{r^2}\cdot\frac{(\mu^2-1)\omega_n+\mu^2}{\omega_n^2}\ . \tag{27}$$

5. *Approximate formulas for calculating r and a from experimental values of R and T_n.* In experimental work, it is possible to determine the reflection in a section of the material of sufficient thickness to allow us to regard the number N of planes contained in it as infinite, that is, R is measured. Then the transmission T_n is measured in a section as thin as possible (n of the order 10^5). Now both r and a are very small (of the order of magnitude 10^{-6}), and a is several times less than r. This suggests writing

$$a/r=\alpha\ , \tag{28}$$

so that $\alpha<1$, and expanding ρ, μ etc. in powers of r. By (1) and (28) we have

$$t=1-(1+\alpha)r\ . \tag{29}$$

whence

$$t^{-1}=1+(1+\alpha)r+(1+\alpha)^2r^2+(1+\alpha)^3r^3+\cdots,$$
$$t^{-2}=1+2(1+\alpha)r+3(1+\alpha)^2r^2+4(1+\alpha)^3r^3+\cdots. \tag{30}$$

It is convenient to introduce the notation

$$\beta=\sqrt{\alpha(2+\alpha)}, \qquad (1+\alpha)^2=\beta^2+1, \tag{31}$$

and from (29) we find

$$\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}=2\beta r\sqrt{1-[(1+\alpha)r-\tfrac{1}{4}\beta^2r^2]},$$

or expanding by the binomial theorem

$$\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}$$
$$=2\beta r\left[1-\frac{1}{2}(1+\alpha)r-\frac{1}{8}r^2-\frac{1}{16}(1+\alpha)r^3-\cdots\right], \tag{32}$$

whence by (20) and (21)

$$(1-r^2)\rho=1-(1+\alpha-\beta)r-\frac{\beta}{2}(1+\alpha-\beta)r^2-\frac{1}{8}\beta r^3-\cdots, \tag{33}$$

$$R=1+\alpha-\beta+\frac{1}{2}\beta(1+\alpha-\beta)r+\frac{1}{8}\beta r^2+\cdots. \tag{34}$$

In the last equation, it is sufficient to retain the constant term, so that $R=1+\alpha-\sqrt{\alpha(2+\alpha)}$, whence, solving for α,

$$\alpha=(1-R)^2/2R, \qquad \beta=1+\alpha-R=(1-R^2)/2R. \tag{35}$$

This determines α in terms of the measured R.[3] To find r from the measured T_n, we expand μ in powers of r by means of (23), (30) and (33):

$$\mu=1+\beta r+\tfrac{1}{2}\beta(1+\alpha+\beta)r^2+\cdots, \tag{36}$$

whence

$$\frac{\mu^2}{\mu^2-1}=\frac{1}{2\beta r}\left[1-\frac{1}{2}(1+\alpha-2\beta)r+\cdots\right]. \tag{37}$$

From (33) and (37) it follows that

$$\frac{\rho}{1-\rho}+\frac{\mu^2}{\mu^2-1}=\frac{1}{r}\left(1+\alpha+\beta+\frac{1}{2\beta}+\cdots\right), \tag{38}$$

[3] Actually, (34) gives α as a power series in r, the constant term being (35), and the next term $(1-R^2)^2/8R^2\cdot r$ which is small enough to be neglected.

where the terms not written out contain the first and higher powers of r. Solving (27) for ω_n, we find

$$\omega_n = \frac{t^2}{2r^2 T_n^2}\left[\mu^2 - 1 + \sqrt{(\mu^2-1)^2 + 4\mu^2 r^2 T_n^2 t^{-2}}\right],$$

where the radical is taken with the plus sign, since ω_n is positive by (24). Using (36) and (30), we find that the lowest term in r inside the bracket is $(2\beta + 2\sqrt{\beta^2 + T_n^2})r$, so that, with the aid of (37),

$$\omega_n + \frac{\mu^2}{\mu^2-1} = \frac{1}{r}\left(\frac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \frac{1}{2\beta} + \cdots\right). \tag{39}$$

Dividing (39) by (38), taking the natural logarithm on both sides and expanding the logarithm of the right hand member in powers of r, we find

$$\log \frac{\omega_n + \dfrac{\mu^2}{\mu^2-1}}{\dfrac{\rho}{1-\rho} + \dfrac{\mu^2}{\mu^2-1}} = \log \frac{\dfrac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \dfrac{1}{2\beta}}{1 + \alpha + \beta + \dfrac{1}{2\beta}} + \cdots.$$

By (25), the expression to the left equals $2n \log \mu$, and since $\log \mu = \beta r + \cdots$ by (36), we finally find, retaining only the lowest powers of r on either side,

$$r = \frac{1}{2n\beta} \cdot \log \frac{\dfrac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \dfrac{1}{2\beta}}{1 + \alpha + \beta + \dfrac{1}{2\beta}}. \tag{40}$$

Since α and β are known by (35), this determines r in terms of the measured T_n, and finally (28) and (29) give $a = ar$, $t = 1 - (1+\alpha)r$.

EVIDENCE FROM CRYSTAL STRUCTURES IN REGARD TO ATOMIC STRUCTURES[1]

By Maurice L. Huggins[2]

Abstract

The distribution of valence electrons in the diamond and similar crystals.—Because of the cubical symmetry, the equivalent scattering power of all the atoms, and the absence of pyro- and piezo-electric effect, the atoms in the diamond cannot be held together as a result of the transfer of electrons from atom to atom. Symmetry requirements also eliminate any cubical arrangement of electrons or orbits around each atom. The diamagnetism of H_2 and of most organic compounds eliminates rotations of two electrons or orbits in the same direction about each atomic center-line as a means of holding the atoms together. Similar structures and numbers of valence electrons, together with interatomic distance comparisons, indicate that the atoms in BeO, ZnO, ZnS, CdS, AgI, etc., are held together in a manner similar to that in the diamond. If so, there cannot be four electrons rotating around each atomic kernel in the diamond, for Zn^{--}, Ag^{---}, O^{++} etc., are chemically impossible. It is not possible for two electrons to be rotating about each two adjacent atomic kernels in crystals of NaCl, MgO, CdO, AgBr, etc., and since chemically and physically these are not very different from BeO, CdS, AgI, etc., the bonds in the last named crystals and so in the diamond are probably not of this type. The conclusion is therefore reached that in the diamond and crystals of similar structure, the electrons are in pairs at tetrahedron corners around each atom, each pair being held jointly by two atoms. This is as predicted from the Lewis theory of valence. A study of the other known crystal structures leads to the conclusion that in general the valence shells of electro-negative atoms are tetrahedra of electron pairs rather than cubes of single electrons.

THIS paper is an attempt to show that important conclusions concerning the ways in which the valence electrons are arranged may be reached from a careful analysis of the structures of some of the simplest crystals.

The diamond. The arrangement[3] of atoms in this substance is pictured in Figs. 1 and 5. Each carbon atom is surrounded by four others placed around it as are the four corners of a regular tetrahedron around its center. All the atoms are equivalent, both as regards their positions

[1] Some of the material given in this paper has been presented at meetings of the American Physical Society and the American Chemical Society. For abstracts, see Phys. Rev., **21**, 379 (1923) and Science, **57**, 534 (1923). The electron distributions arrived at were proposed by the author in the J. Am. Chem. Soc. **44**, 1841 (1922).

[2] National Research Fellow.

[3] See Wyckoff, "The Structure of Crystals," Chem. Cat. Co., New York, 1924, for references to the crystal structure work.

in the structure and their ability to scatter x-rays. The symmetry of the structure, as shown by both the crystallographic and the x-ray data, is that of the cubic or isometric system.

There are four valence electrons per atom; our problem is to determine, if possible, how they are distributed.[4] The tetrahedral arrangement around each atom, the stability of the diamond toward disruption by heat or chemical action, its low electrical conductivity, etc., suggest that the atoms in this crystal are held together in the same manner as the carbon atoms in "saturated" organic compounds.[5] The theories which have been proposed for the nature of such a union may be divided

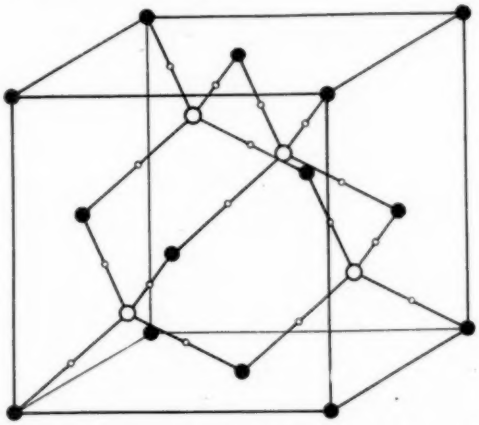

Fig. 1. Unit cube of the diamond, cubic ZnS, etc. In the diamond all atoms are of carbon and the electron pairs, represented by the small circles, are at the mid-points of the atomic centerlines, as shown. In ZnS the Zn atoms are in the positions represented by the large dots, the S atoms are in those represented by the large circles, and the electronpairs are on the centerlines between atoms, but closer to the sulfur than to the zinc.

into two classes, (1) those assuming the transfer of electrons from atom to atom,[6] the individual carbon atoms being represented as $^{+}_{+}C^{+}_{+}$, $^{+}_{+}C^{+}_{-}$,

[4] It would also be of interest to learn how the two K electrons of each atom are placed, but the evidence at hand is insufficient to enable us to do this. The symmetry and x-ray requirements are met if they are so close to the nuclei as not to affect appreciably the symmetry of the arrangement of valence (L) electrons, and either are oriented relative to their nuclei in a random way throughout the crystal or are regularly distributed in a large unit having cubic symmetry.

[5] Such interatomic distance data as are at present available for crystals of organic compounds are also in agreement with this idea. If correct, then the conclusions to be drawn regarding the type of atom-bonding in the diamond are also applicable to the bonds within organic molecules.

[6] Thomson, "The Corpuscular Theory of Matter," Scribner, New York, 1907; Falk and Nelson, J. Am. Chem. Soc. **32,** 1637 (1910); Fry, Zeits. f. Phys. Chem. **76,** 385 (1911); J. Am. Chem. Soc. **34,** 664 (1912); Stieglitz, ibid, **44,** 1293 (1922).

$\overset{+}{-}C\overset{+}{-}$, $\overset{+}{-}C\overset{-}{-}$, or $\overset{-}{-}C\overset{-}{-}$; and (2) those postulating the sharing of electrons between atoms.[7]

Considering now the first of these classes, if the atoms in the diamond were half $\overset{+}{+}C\overset{+}{+}$ and half $\overset{-}{-}C\overset{-}{-}$ they would not have equivalent scattering powers, for those of the first kind would have but two electrons each, while those of the latter would have ten. Furthermore, the [111] faces of the crystal would be electrically polar, the layers of atoms parallel to these faces being alternately positive and negative and spaced as indicated in Fig. 2. This would be made manifest by the presence of

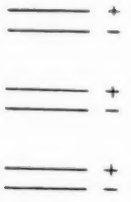

Fig. 2. Spacing of [111] planes in ZnS (also in the diamond, if the atoms were charged).

pyro-electric and piezo-electric effects, as in ZnS, for instance. The same objections apply to a structure consisting of $\overset{+}{+}C\overset{+}{-}$ and $\overset{+}{-}C\overset{-}{-}$ atoms, arranged so that each carbon-carbon bond is positive at one end and negative at the other; there is also the additional objection that the distribution of charges would have the symmetry of the trigonal system rather than that of the cubic or regular system. This would result not only in displacement of the atomic centers in the direction of the three-fold symmetry axis, but in irregular growth, unsymmetrical etch figures, interference figures (produced by polarized light) indicative of the lower symmetry, etc. If all the atoms in the crystal were $\overset{+}{-}C\overset{+}{-}$, held together by electrostatic forces concentrated at the "ends of the bonds," the crystal would have tetragonal symmetry and the [001] faces would be polar, as the positive ends of all the atoms would be turned in the same direction. We thus arrive at our first conclusion, that *the atoms in the diamond are not held together as a result of the transfer of electrons from one atom to another.* This must be true whether the electrons are in or vibrating about fixed positions in the atoms, or are revolving in orbits.

[7] Lewis, J. Am. Chem. Soc. **38**, 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923; Bohr, Phil. Mag. **26**, 857 (1913).

According to the electron-sharing theory, which chemists[8] have found exceedingly useful in accounting for the properties of substances containing non-polar bonds, the kernel of an electronegative atom tends to be surrounded by a valence shell containing eight electrons, and in order to accomplish this result it bonds with other atoms, two electrons (or electron orbits) shared between two atoms constituting a typical "single bond." The eight electrons of a complete shell were at first represented as at corners of a cube, but, in order to account for the triple bond of organic chemistry and for other reasons, the "cubical atom" was later abandoned in favor of the "tetrahedral atom," in which the valence electrons are assumed to be drawn together in pairs.[9]

If each atom in the diamond had a valence shell consisting of a cube of single electrons or electronic orbits (Fig. 3), the crystal would have

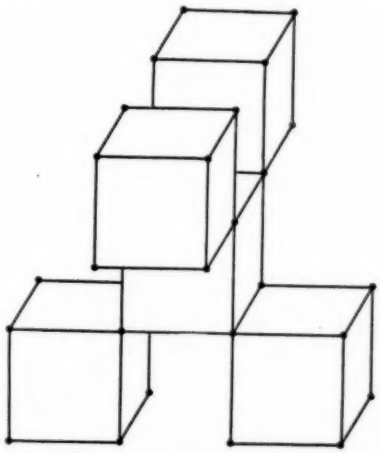

Fig. 3. Cubes edge to edge in a pseudo-diamond type of structure having tetragonal symmetry. The small dots represent single valence electrons.

tetragonal symmetry, for the arrangement in the direction of one of the crystal axes would be different from that in the direction of each of the other two axes. The ratio of the unit distances would be $1:1:\sqrt{2}$, rather than 1:1:1, as is actually the case. *No cubical arrangement of electrons or electron orbits around each atom, with two electrons or orbits shared between each two adjacent atoms, could give a structure for the diamond having the symmetry of the cubic system.*

The minimum elements of symmetry which a crystal must possess in order to belong to the cubic system[10] are four three-fold symmetry

[8] Lewis, Ref. 7; Langmuir, J. Am. Chem. Soc. **41**, 868, 1543 (1919); **42**, 274 (1920); Latimer and Rodebush, ibid. **42**, 1419 (1920); Huggins, ibid. **44**, 1607 (1922).

[9] Lewis, Ref. 7; Huggins, J. Phys. Chem. **26**, 601 (1922).

[10] See any good book on crystallography.

axes and three two-fold symmetry axes. As the observations used to determine the symmetry of crystals—the symmetry of the diffraction effects with light and with x-rays, the rates of growth and solution in different directions, etc.—depend largely (in case of the diamond at least) on the distribution of the valence electrons, we may say with certainty that their distribution must either possess the elements of symmetry just mentioned or there must be a randomness in the arrangement which statistically will produce the observed effects. Inspection of the arrangement of atomic centers in the diamond shows that a distribution of *pairs* of electrons tetrahedrally about each atomic kernel satisfies the symmetry requirements just mentioned, *provided both electrons of each pair are on, or distributed in a random manner about, the straight line connecting the two nearest atomic centers.* The corresponding requirements which must be satisfied by a distribution of electron *orbits* in the diamond may be stated as follows: *Fixed (non-precessing) orbits, other than circular orbits in planes normal to the three-fold axes, are impossible, unless oriented in a random manner about these axes. If there are electron rotations or orbital precessions, they cannot be synchronized with each other throughout the crystal.* If the synchronization were such as to produce one true three-fold symmetry axis there could be no other similar axes in the crystal. In other words, it is impossible to build up any crystal having the cubic symmetry which the diamond is known to possess with *fixed* orbits or *synchronized* precessions or rotations.

Considering now the types of orbital motions not ruled out by the arguments in the foregoing paragraphs, we might imagine adjacent carbon atoms to be held together as a result of rotations of electrons or of orbits about the atomic center-line in one of the ways represented in Fig. 4.[11] If the first were correct, though, and the same type of bonding exists in organic molecules, a large majority of the latter should be paramagnetic. A compound like methane, $H:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:H$, we might expect to be diamagnetic, but it would seem very unlikely that in ethane, $H:\ddot{\underset{\ddot{H}}{C}}:\ddot{\underset{\ddot{H}}{C}}:H$, or in propane, $H:\ddot{\underset{\ddot{H}}{C}}:\ddot{\underset{\ddot{H}}{C}}:\ddot{\underset{\ddot{H}}{C}}:H$, for instance, the magnetic effect of each pair could be counterbalanced by the effects of the others. The same argument would of course also apply to molecular hydrogen, if the atoms were held together in the manner of Fig. 4A.[12]

[11] Cf. Lewis, "Valence, Etc." (Ref. 7) p. 59.

[12] Cf. Bohr, Ref. 7.

Moreover, if the bonds in the diamond were of this type, there would be two kinds of atoms. In one all rotations would be clockwise, in the other counter-clockwise, as seen from the center of the atom. (If each atom contained both clockwise and counter-clockwise rotations, the crystal would have trigonal or tetragonal symmetry, as was shown would be the case if the atoms contained both plus and minus charges $-\overset{+}{-}C\overset{+}{-}$ or $\overset{+}{-}C\overset{-}{-}$ and $\overset{+}{+}C\overset{+}{-}$.) Atoms of the first kind could only combine with those of the second kind, and vice versa. If they were held together as indicated in Fig. 4B, all the atoms in a single crystal would be of the same kind, having all the rotations (of the nearest valence electrons) clockwise, for instance, as viewed from the atomic center. There is of course no *a priori* reason for assuming that counter-clockwise atoms could not exist, but they would have to be in a different crystal, for only atoms of like rotational character could combine together. Either

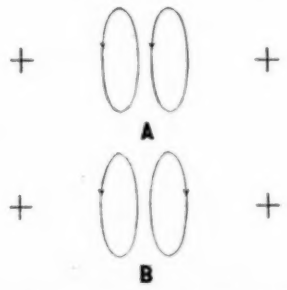

Fig. 4. Representing two types of rotations of valence electrons or orbits about atomic centerlines.

of these two hypotheses would lead to rather fantastic conclusions with regard to organic reactions, but further discussion of this subject is beyond the scope of this paper.

It might be noted in addition that from ordinary electromagnetic theory we should expect repulsion between two electrons of a pair rotating as in Fig. 4B. This would also be true, except in the case of ring electrons, if the electrons were rotating as in Fig. 4A.

In order to proceed further with the elimination of proposed types of interatomic bonds, we shall now consider other closely related structures.

Crystals having structures similar to that of the diamond. Silicon,[13] germanium,[3] and gray tin[3] have been found to have crystal structures of the same type as the diamond. Each of these elements is tetravalent and it seems reasonable to assume four valence electrons per atom and

[13] Ref. 3. Küstner and Remy, Phys. Zeits. **24**, 25 (1923).

that the atoms are held together in the same way as are the carbon atoms in the diamond. Insofar as the chemical and physical properties of these substances are known, they are in accord with these conclusions. The binary compounds ZnS[3], ZnSe[14], ZnTe[15], HgS[16], HgSe[15] HgTe,[15] CdTe[15], CuCl[3], CuBr[3], CuI[3], AgI[3], and AlSb[17], also have the same type of structure, half of the atoms of course being of one kind and half of the other. In ZnS, for example, each zinc atom is surrounded by four sulfur atoms at corners of a regular tetrahedron and each sulfur similarly by four zinc atoms (Figs. 1 and 5).

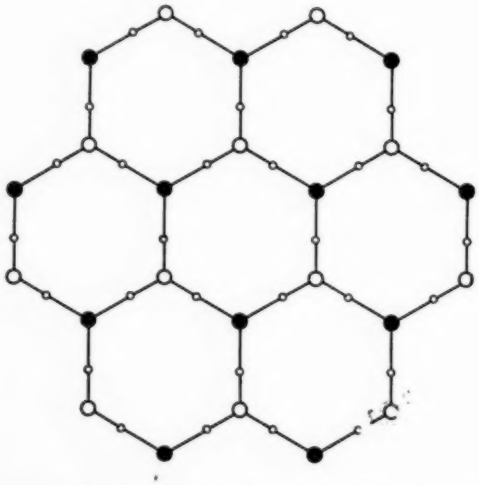

Fig. 5. Representing the distribution of atoms and electronpairs within each layer in crystals of the diamond, ZnS, and ZnO types. The large dots and large circles denote atoms in different planes. In the diamond, Si, etc., all atoms are of the same kind and the electronpairs (small circles) are midway between atomic centers: in ZnO, ZnS, etc., the dots represent atoms of one kind and the large circles those of another, the electronpairs being closer to one kind of atom than to the other, as shown. In crystals of either type each atom is also bonded to another, directly over or under it, in another layer.

A number of other binary compounds, namely AlN[18], BeO[3], ZnO[3], ZnS[3], ZnSe[15], CdS[19], CdSe[15], and AgI[3], possess structures which, although they have the symmetry of the hexagonal system, resemble the cubic structures just mentioned in that each atom is surrounded

[14] Huggins, Phys. Rev. **21**, 211 (1923). Davey, ibid. **21**, 380 (1923).
[15] Huggins, Ref. 14.
[16] Huggins, Ref. 14. Kolkmeijer, Bijvoet and Karssen, Proc. Acad. Sci., Amsterdam, **27**, 390 (1924); Verslag Akad. Wetenschappen **33**, 327 (1924).
[17] Owen and Preston, Proc. Phys. Soc., **36**, 341 (1924).
[18] Ott, Zeits. f. Phys. **22**, 201 (1924).
[19] Ref. 3. Huggins, Ref. 14.

tetrahedrally by four others of opposite character (Cf. Fig. 5). This is probably also true of carborundum (SiC)[20].

In the cubic structures listed above, the tetrahedron of atoms closest to any given atom *must* be regular; in the hexagonal crystals it is also very nearly regular (at least within a percent or two, approximately the limit of error of the experimental determinations). Moreover, in those cases (e.g. ZnS and AgI) in which the same chemical compound crystallizes in both ways, the distance between adjacent atoms (Table I) is almost identically the same in the two crystals.

TABLE I

Interatomic distances in various crystals

Crystal	Distance	Reference
C	1.54A	Bragg[3], Hull[3]
Si	2.34–2.36	Debye and Sherrer[3] Hull[3], Gerlach[3], Küstner and Remy[13]
Ge	2.43; 2.44	Kolkmeijer[3], Hull[3]
Sn	2.80	Bijl and Kolkmeijer[3]
SiC	1.90	Ott[20]
AlN	1.89	Ott[18]
AlSb	2.65	Owen and Preston[17]
BeO	1.65	McKeehan[3]
ZnS, cubic	2.34; 2.35	Gerlach[3], Bragg[3]
ZnS, hexagonal	2.33; 2.36	Aminoff[3]; from density=3.98 (Mourlot[21])
ZnSe	2.45; 2.43	Davey[3]; from density=5.40 (Margottet[22])
ZnTe	2.53	From density =6.34 (Margottet[22])
CuCl	2.32; 2.38	Davey[3]; Wyckoff and Posnjak[3]
CuBr	2.49; 2.52	Davey[3]; Wyckoff and Posnjak[3]
CuI	2.61; 2.63; 2.64	Aminoff[3]; Davey[3]; Wyckoff and Posnjak[3]
AgI, cubic	2.81; 2.83	Wilsey[3]; Davey[3]
AgI, hexagonal	2.81	Aminoff[3]; Wilsey[3]

This, together with the further fact that the physical and chemical properties of the two forms are all almost exactly the same, shows that the atoms in both must be held together in the same way.

If we follow Thomson,[6] Lewis,[7] Kossel,[23] Bury,[24] Bohr,[25] Huggins,[9] Stoner,[26] and others in assigning one valence electron to each atom of an element in Group I of the periodic table, two electrons to each atom of an element in Group II, etc., we find that in all of these crystals there is an average of four electrons per atom, the same as in the diamond, Si, Ge, and Sn. Moreover, as shown by Table I, pairs of crystals

[20] Ott, Naturwissenschaften **13,** 76 (1925). See also Ref. 3.
[21] Mourlot, Ann. d. chim. Phys. **17,** 534 (1899).
[22] Margottet, Compt. rend. **84,** 1293 (1877).
[23] Kossel, Ann. der Physik, **49,** 229 (1916).
[24] Bury, J. Am. Chem. Soc. **43,** 1602 (1921).
[25] Bohr, Zeits. f. Physik **9,** 1 (1922).
[26] Stoner, Phil. Mag. **48,** 719 (1924).

with similar physical and chemical properties (diamond and BeO, Ge and ZnSe, Sn and AgI, and SiC and AlN) have nearly the same interatomic distances.

It seems highly probable then that *the atoms in all of these compounds are held together in a way which is not radically different from that in the diamond*. Any theory of the nature of the bonds between the atoms must be applicable to all of these compounds without necessitating any abrupt change from one type of bond to another. *It would therefore seem very unlikely that in zinc sulfide, for instance, all the valence electrons are in rotation in orbits enclosing the sulfur kernel with none enclosing the zinc kernel*, for such a distribution (of *all* the electrons about *half* the atoms) was shown to be impossible in the diamond, and an abrupt change would be necessitated in going from such a structure to one in which four electrons were rotating around each kernel. By similar reasoning *we must consider extremely improbable any arrangement of four electrons rotating about each atomic kernel* in the diamond, for such a structure for ZnS, BeO, or AgI would require such chemically absurd ions as Zn^{--}, Ag^{---}, O^{++} etc. Moreover, no structure placing but two electrons about each electropositive atom and six about each electronegative atom (in ZnS or BeO) is possible, because a corresponding electron distribution in the diamond could not be correct.

Crystals having the sodium chloride type of structure. The following compounds have been found to have the type of atomic arangement pictured in Fig. 6: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, RbBr, RbI, CsF, MgO, MgS, CaO, CaS, CaSe, SrO, SrS, SrSe, BaO, BaS, BaSe, MnO,[27] MnS, CdO, NiO, CoO, PbS, AgCl, and AgBr.

If we again assume current theories[28] in regard to the number of valence electrons to be correct, we find in each case,[29] as before, an average of four per atom. In these crystals, however, there are *six* equivalent electronegative atoms around each electropositive atom and vice versa, and it is not structurally possible for the atoms to to be held together by electrons rotating in orbits enclosing two nuclei. If the bonds between atoms were of this type in the crystals having structures like the diamond, ZnS and ZnO, we should then expect very decided differences in properties between the two classes of substances. When we compare the properties[30] of BeO and MgO, of CdO and CdS, or of

[27] Levi, Gazz. chim. ital., **54**, 704 (1924).
[28] Ref. 6, 7, 23, 24, 25, 26.
[29] Except, perhaps, in PbS.
[30] See any standard work on inorganic chemistry.

AgBr and AgI, we find no such marked differences. *This observation eliminates from further consideration any structure*, for any of the crystals so far discussed, *in which the atoms are held together by valence electrons in rotation about two atomic centers.*

We have then no alternative but to conclude that, provided the arguments used in the foregoing analysis are valid, *the valence electrons in the diamond and crystals of similar structure*, including those of the zinc oxide type, *are in pairs at tetrahedron corners around each atomic kernel, each electron pair being held jointly by two atoms.* Whether the electrons are in, or oscillating about, equilibrium positions on the atomic centerlines, or are ring electrons or electrons rotating in orbits about these

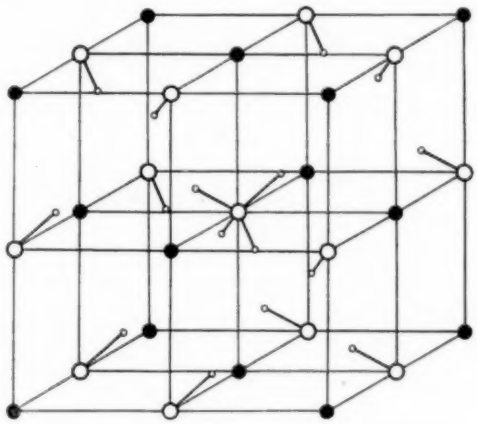

Fig. 6. Unit cube of the sodium chloride structure, showing the probable distribution of the valence electronpairs. The large dots represent sodium kernels and the large circles chlorine kernels. Atoms of either kind, considered separately, are at the points of a face-centered cubic lattice.

centerlines (in the relative directions indicated in Fig. 4B) need not be further discussed at this time.

It has not been shown whether the valence electrons in crystals of the sodium chloride type are in pairs at tetrahedron corners, or singly at cube corners, around the kernels of the electronegative atoms. Certainly, if we had only crystals of this type to consider, the cubical arrangement would seem more likely than the tetrahedral, but the fact that in all the other crystals discussed in this paper and in many more to be dealt with in another article[31] the kernel of each electronegative atom must be surrounded by a tetrahedron of electronpairs makes it seem very probable that this is also the case in these crystals (Fig. 6).

[31] Soon to be published.

As the valence electrons are surely much more tightly held by the kernels of the electronegative atoms (within the valence tetrahedra) than by those of the electropositive atoms, it is often convenient, and an approximation to the truth, to speak of the structure as composed of electropositive and electronegative "ions." Similarly we may speak of the "ions" of beryllium and oxygen in a crystal of BeO, but in either case it should be understood that the valence electrons have not passed *completely* from one atom to another but are mutually held by two or more atoms, also that all degrees of "ionization" (or better, "polarity") are possible, these substances and the diamond being extreme cases.

Other crystals. A study[31] of other crystals of known structure has resulted in the following conclusions:

(1) *In all those which contain electronegative atoms*, excepting only $CsICl_2$, graphite, and certain carbonates and nitrates, *the arrangement is such as to permit a valence shell of 8 electrons around the kernel of each electronegative atom.*

(2) In those which contain electronegative atoms adjacent to each other, excepting only $C(CH_2OH)_4$ and the crystals just mentioned as exceptions to the preceding generalization, valence shells consisting of tetrahedra of electronpairs are possible in full accord with all available data, while cubic valence shells are in FeS_2, MnS_2, Se and Te improbable and in all other cases impossible.

(3) In those containing both electropositive and electronegative atoms, with the latter not adjacent to each other, a comparison of the structures obtained on the assumption of tetrahedral valence shells with those obtained on the assumption of cubical valence shells favors the former as the more probable in nearly every case.

(4) In crystals of the metals, the prevailing tendency seems to be for each atom to surround itself by as many others as possible, the number of valence electrons and the orienting tendencies of the atomic kernels being of minor importance.

In view of the above, it would seem reasonable to assume a tetrahedron of electronpairs as the valence shell of each electronegative atom, whenever such an assumption is not in conflict with x-ray or other evidence. The probable electronic distributions so obtained will be dealt with in detail in another paper.[31]

The Cause of Pairing. Although the author believes that the evidence given in this paper conclusively proves the existence of electronpairs in atomic shells, he is not able to give any satisfactory reason for their existence. There seem to be two alternatives; either there must be an attractive force between electrons at small distances, or the repulsion

between electrons must rapidly decrease with decrease in distance, for distances less than a certain value. The latter alternative would not require electronpairing except in atomic shells, but would qualitatively at least account for the formation of pairs and for the grouping of electrons into distinct shells.

In conclusion the author wishes to express his thanks to Professor D. L. Webster of Stanford University for his valuable criticism.

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BAND SERIES IN INFRA-RED ABSORPTION SPECTRA OF ORGANIC COMPOUNDS. I

By Joseph W. Ellis

Abstract

The frequencies of a series of outstanding absorption bands characteristic of organic liquids, previously attributed by the author to vibrations between atoms of a carbon-hydrogen pair, are shown to fit the equation,

$$\nu_n \cdot 10^{-12} = 47.37n - 0.783n^2,$$

where $n = 1, 2, \ldots\ldots, 10$. Many of the bands of secondary intensity in the spectra of compounds containing a carbon-carbon bond have their frequencies expressed by

$$\nu'_n \cdot 10^{-12} = 10.71n.$$

where $n = 1, 2, \ldots\ldots, 28$. Practically all other bands observed below 7μ in such spectra can be accounted for by combinations of low frequency members of these two series, $\nu_c = \nu_m + \nu_n'$. Measurements on bands occurring between 2μ and 3μ were made from records obtained with a new registering spectrograph. A number of such spectra are shown.

FOR a decade and a half following the publication by Coblentz[1] of his extensive monograph on infra-red absorption and emission spectra, comparatively little work was done in infra-red spectroscopy, especially in the study of absorption by organic compounds. During this period, however, Weniger[2] published his results of an investigation of a number of alcohols; Johnson and Spence[3] studied a number of aniline dyes, and Stang[4] investigated the absorption of naphthalene and some of its derivatives dissolved in carbon disulfide and carbon tetrachloride.

The origins of the great number of absorption bands observed in such investigations have remained practically unexplained. Puccianti,[5] in a short but accurate and important investigation, discovered a band near 1.71μ occurring in all of the fifteen carbon-hydrogen compounds which he had examined, and attributed it to a C-H group. Coblentz[1] had observed a few bands bearing multiple wave-length relationships to be characteristic of groups of compounds, and assigned as the origin

[1] Coblentz, "Investigations of Infra-red Spectra" (1905).
[2] W. Weniger, Phys. Rev. **31**, 388 (1910).
[3] Johnson and Spence, Phys. Rev. **5**, 349 (1915).
[4] Stang, Phys. Rev. **9**, 542 (1917).
[5] Puccianti, Nuovo Cim **11**, 141 (1900); Phys. Zeits. **1**, 48 (1899); **1**, 494 (1900).

of such bands groups within the molecule, as the alkyl groups CH_2 and CH_3.

Interest is again being aroused in the study of absorption spectra of organic compounds with a view to explaining the numerous bands which characterize them. Lecomte,[6] in a series of short articles, gives results, obtained with a Hilger infra-red wave-length spectrometer, of an investigation of many types of compounds. He concludes that the bands originate from vibrations within the molecule rather than of the molecule as a whole. In particular, he concludes that absorption due to the carbon atoms is but little dependent upon the type of carbon chain. Bell[7] has recently carefully determined the absorption between 2μ and 12μ of aniline and ten alkyl anilines, and finds that, among the numerous bands which occur, one at 2.8μ is characteristic of the amino group. Two years ago the writer[8] published in this journal the results of an investigation of the absorption spectra of thirty-one organic liquids to 2.5μ, obtained with a self-registering flint glass spectrograph of high dispersion. The liquids studied were benzene, toluene, p-xylene, mesitylene, pentane, hexane, heptane, octane and several halogen derivatives of methane, ethane, propane and butane. The investigation showed great similarities among these spectra. Márton[9] has just published the results of an investigation, which he began before the above work was published, in which he independently arrived at some of the author's earlier conclusions, which will be reviewed later in this article.

An examination of the spectrum curves presented in both the early and later investigations reveals two facts which suggest that the absorption bands may be arranged in series originating in the longer wave-length region, whose members suffer gradual diminution of intensity and increasingly shorter wave-length separations as the series progresses toward the limits of the visible spectrum. These facts are:

1. For investigations in the region between 15μ and 3μ best results are obtained when absorbing thicknesses of 0.1 mm or less are used; for the regions between 3μ and 2μ and 2μ and 1μ, cells of 1 mm and 10 mm respectively yield best results; while to bring out clearly the bands between 1μ and the visible red, cells of about 100 mm thickness have to be used.

2. There are relatively fewer bands in the longer than in the shorter wave-length region.

[6] Lecomte, Compt. Rend. **178,** pp. 1530, 1698, 2073 (1924); **180,** 825 (1925).
[7] F. K. Bell, J. Am. Chem. Soc. **47,** 2192 (1925).
[8] Ellis, Phys. Rev. **23,** 48 (1924).
[9] Márton, Zeits. f. Phys. Chem. **117,** 97 (1925).

The complexity of the absorption curves increases more with an increase in the number of distinct types of atoms within the absorbing molecule than with the general complexity, or size, of the molecule itself. This suggests that the origin of the different absorption bands may be traced to definite atoms, or pairs of atoms, as absorbing centers.

A theory of infra-red absorption which would explain all of the bands of very long wave-length as originating from pure rotational effects of the molecule and all of the shorter wave-length bands as due to a combination of rotations and linear vibrations has met with some success in the cases of some relatively simple gas molecules. The series of regularly spaced bands in the long wave-length region of water vapor spectra found by Rubens[10] and Fr. von Bahr[11] has been considered an example of the effects of pure rotation of a molecule in the absorption of radiant energy. A second, and more recent, example of a pure rotation spectrum is the series of regularly spaced absorption bands of HCl found by Czerny[12] between 40μ and 80μ. Such rotations have been quantized, and infra-red bands due to them are assumed to originate from discrete changes among the possible states of rotation, the angular momenta of these states bearing integral ratios to one another.

The second type of absorption, first proposed by Bjerrum,[13] predicts that bands in the short wave-length region should be double, and that when studied with a spectroscope of high resolving power each branch should appear made up of equally spaced lines, whose separations should be equal to those of longer wave-length bands of the purely rotational type. Such serrated bands had already been observed by Rubens[10] and Fr. von Bahr[11] in the cases of water vapor and HCl gas, but the first precision measurements were made on the former gas by Sleator,[14] and in the case of HCl and also HF and HBr, by Imes.[15] The separation of Czerny's long wave-length bands for HCl are equal to those found by Imes in the fine line structure of the near infra bands, thus confirming, in this case, Bjerrum's theory. Bands of the latter type have recently been measured in the spectrum of ammonia by Spence,[16] and in the spectrum of methane by Cooley.[17]

[10] Rubens, Berliner Ber., page 513 (1913).
[11] Eva von Bahr, Verh. d. Deutsch. Ges. **15,** pp. 731, 1150 (1913).
[12] Czerny, Zeits. f. Physik **34,** 227 (Sept. 28, 1925).
[13] Bjerrum, Verh. d. Deutsch. Ges. **16,** 737 (1914).
[14] Sleator, Astrophys. J. **48,** 124 (1918).
[15] Imes, Astrophys. J. **50,** 251 (1919).
[16] Spence, J.O.S.A. and R.S.I. **10,** 127 (1925).
[17] Cooley, Astrophys. J. **52,** 73 (1925).

The frequencies of the centers of bands of this type are determined by the discrete modes of vibration of the molecule, and at least in the case of diatomic molecules these bands should appear in series whose members have approximately equal frequency spacings. This has been found to be the case, although but few bands have ever been found for any one gas. Such bands are not exactly equally spaced, but rather have their frequencies expressed by the formula,

$$\nu_n = n\nu_0(1-nx), \tag{1}$$

where ν_0 and x are constants for a given substance and $n = 1, 2, 3$, etc. This formula has been developed for such cases by Kratzer[18] on the basis of the non-linearity of the law of force which holds between bonded atoms.

An advance has been made in the case of water vapor by Hettner,[19] who has been able to account for the numerous observed absorption bands on the basis of two frequency series and simple additive combinations of members of these series.

It will be noticed that, unlike the ordinary optical spectral series, series of the above type never converge, although their wave-length differences become relatively small, even between members not far from the beginning of the series.

It would seem that we might expect series, similar to the ones characteristic of gases, in the absorption spectra of liquids and solids, although it might be doubtful whether a high resolving power should reveal any duplicity or fine line structure within the bands. The few multiple relations found by Coblentz in his investigations of organic liquids suggest such series. Schaefer and Thomas[20] have shown that all crystalline sulfates have four characteristic absorption frequencies which form a linear series, and the author[21] has found that calcium sulfate has two additional bands which form the fifth and sixth members of such a series.

A C-H Series

In an investigation[8] mentioned above the writer showed that all the organic liquids which he investigated had several absorption bands at approximately the same wave-length values. The average values of these wave-lengths for the thirty-one compounds studied in cells of 11 mm thickness are: 0.913μ, 1.023, 1.171, 1.375 and 1.695. As a con-

[18] Kratzer, Zeits. f. Physik **3**, 289 (1920).
[19] Hettner, Zeits. f. Physik **1**, 351 (1920).
[20] Schaefer and Thomas, Zeits. f. Physik **12**, 330 (1923).
[21] Ellis, J.O.S.A. and R.S.I. **8**, 1 (1924).

tinuation[21] of this study, a number of compounds were also examined in cells of approximately ten times this thickness, and in each case two new bands appeared, the mean wave-length values of which are 0.760μ and 0.835μ. Among the various compounds these seven bands vary slightly in position, although in no case is there a variation from the mean greater than three percent. These bands are the most outstanding ones of the spectra, but in many cases they have superposed, or partially superposed, upon them minor bands which tend to shift their maximum absorption points from their true positions. Consequently, in searching for series relations among such bands their mean values should be used.

It was shown that the corresponding frequency values of these bands could be quite accurately expressed as a non-linear series by means of formula (1), which had been developed for gases by Kratzer from theoretical considerations. The values of n in this instance vary from 4 to 10 inclusively. The constants, ν_0 and $\nu_0 x$, were calculated for seven substances. Since this formula was developed upon the assumption that the absorption was due primarily to the oscillations of a pair of atoms, constituting the diatomic gas molecule, it is natural to assume in the case of liquids that the absorption originates from oscillations of a linked pair of atoms within the rather complex molecule. The only type of such a linkage in common to all the substances investigated was a C-H bond, and the above series was attributed to this pair, and may be called a carbon-hydrogen, or C-H series.

Formula (1) may be expressed in terms of two constants, A and B,

$$\nu_n = An - Bn^2, \tag{2}$$

which is a special form of the general parabolic formula which characterizes many phases of band spectra. A and B have been calculated from the average observed frequencies of all the bands observed in the investigation mentioned above, and have the following values:

$$A = 47.37 \times 10^{12}$$
$$B = 0.783 \times 10^{12}$$

The accuracy with which the formula,

$$\nu_n \times 10^{-12} = 47.37n - 0.783n^2 \tag{3}$$

expresses the observed frequencies is shown in Table I.

Extrapolation of formula (3) to include $n = 3$, 2 and 1 indicates that bands should be found at 2.22μ, 3.28μ and 6.44μ. The last two lie within the region which must be examined with rock salt spectroscopes, and the writer has already pointed out that bands appearing near 3.4μ

TABLE I

Calculated and observed (average) bands of a C-H series.

n	$\nu\times10^{-12}$ (calc.)	$\nu\times10^{-12}$ (obs.)	λ(calc.)	λ(obs.)
10	395.4	394.8	0.758μ	0.760μ
9	363.0	361.5	0.827	0.835
8	328.8	328.8	0.913	0.913
7	293.4	292.8	1.022	1.023
6	255.9	256.0	1.172	1.171
5	217.5	218.1	1.379	1.375
4	177.0	177.0	1.695	1.695
3	135.2		2.22	
2	91.6		3.28	
1	46.6		6.44	

and 6.8μ in Coblentz's curves are probably to be identified as these bands. Bands near 2.22μ have usually appeared in most investigations, but the writer has shown in the present study that there are several

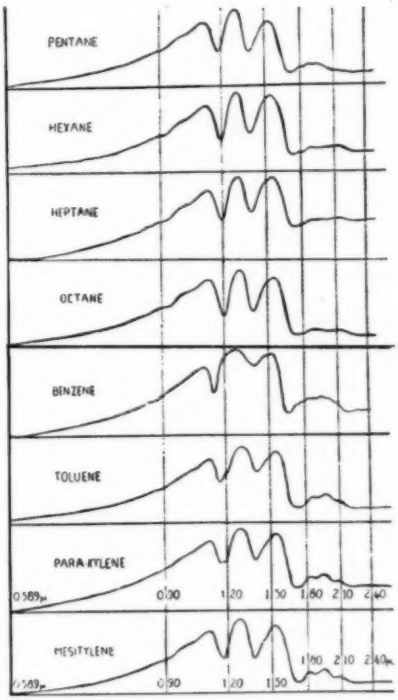

Fig. 1. Absorption spectra to 2.5μ obtained with a registering glass spectrograph. Thickness of cells was 11 mm.

bands in this region, making the exact location of the third member of the C-H series uncertain.

In his recent report Márton[9] also concludes that his observed bands are expressible by an equation similar to (1), and points out that the first member should occur near 6.5μ. He makes no attempt, however, to identify this series with any group within the molecule.

A C-C Series

Fig. 1 shows the absorption spectra to 2.5μ, previously published in this journal,[8] of a few relatively simple carbon compounds of both the aromatic and paraffin series. It will be noticed that in addition to the prominent members of the C-H series there are a number of minor bands. These have never been accounted for but an attempt is made in the present work to account for them on the basis of a single-bonded C-C series and simple combinations between this and the C-H series.

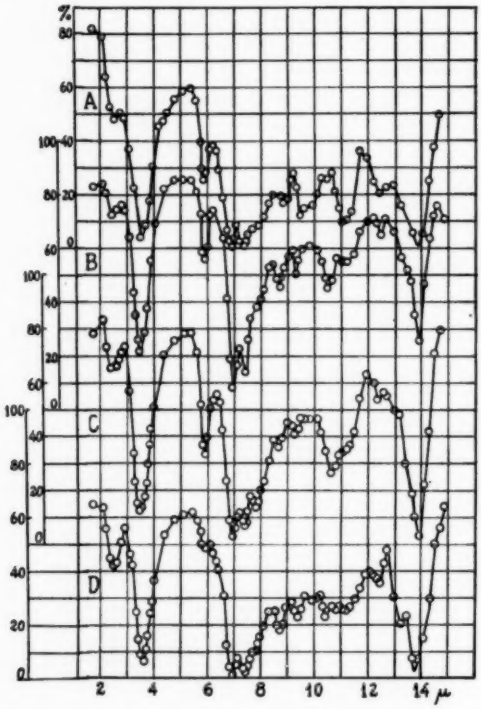

Fig. 2. Spectra obtained by Coblentz with a rock salt spectroscope.
A—0.24mm hexane C—0.15mm dodecane
B—0.15mm octane D—0.15mm hexadecane

Fig. 2 gives a reproduction of some of Coblentz's typical spectra[22] of compounds of the paraffin series, while Fig. 3 gives similar spectra for members of the benzene series. After the bands at 3.4μ and 6.8μ common

[22] Published by permission of the Carnegie Institution of Washington.

to these substances, probably the most striking feature is a deep band near 14μ. If we take this as the beginning of a C-C series we meet with only partial success in accounting for the numerous secondary bands of the shorter wave-length region. But if we assume that such a series originates at 28.0μ, a region never investigated for such substances, we can account for these bands in a relatively simple manner.

Such a series would predict a number of bands in the region between 2μ and 3μ. To search for these, and others, a new self-registering

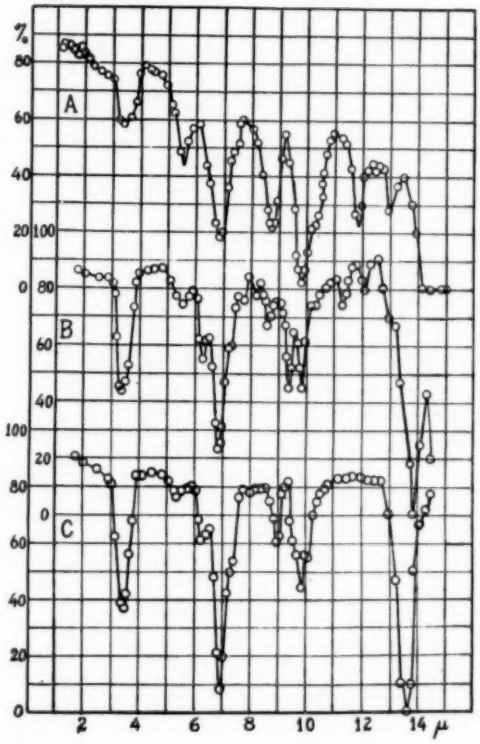

Fig. 3. Spectra obtained by Coblentz with a rock salt spectroscope.
A—0.16mm benzene
B—0.01mm toluene
C—0.01mm o-xylene

spectrothermograph, recently described by the author,[23] has been assembled. This is equipped with quartz prisms, the combined refracting angles of which are equivalent to 180°. This instrument, although the prisms are small, has a fairly high dispersion.

Figs. 4 and 5 show the spectra of several compounds obtained for the region between 2μ and 3μ with this machine. The dotted tracing

[23] Ellis, J.O.S.A. and R.S.I. **11**, (December 1925).

above the absorption curve of p-xylene is an approximation of the original distribution of energy. The atmospheric carbon dioxide band

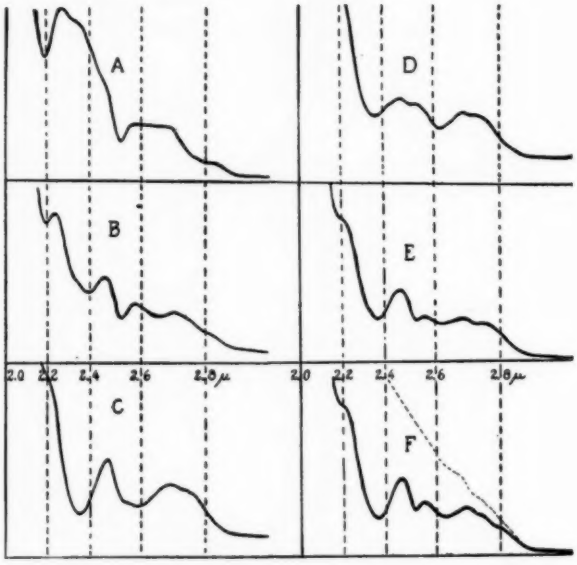

Fig. 4. Absorption spectra obtained with a registering quartz spectrograph.

A—0.05mm benzene	D—0.05mm o-xylene
B—0.05mm toluene	E—0.05mm m-xylene
C—0.05mm mesitylene	F—0.05mm p-xylene

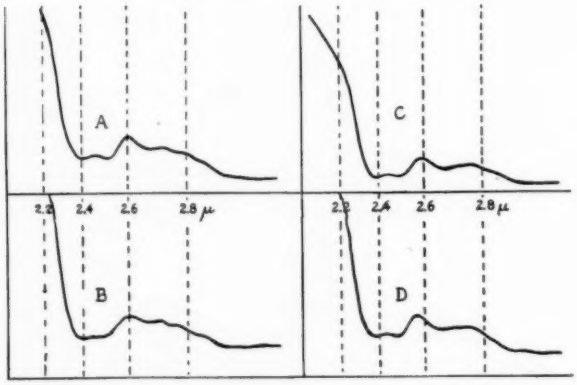

Fig. 5. Absorption spectra obtained with a registering quartz spectrograph.

A—0.05mm pentane	C—0.05mm octane
B—0.05mm hexane	D—0.05mm decane

at 2.73μ and the water vapor band at 2.66μ always appear in such a distribution curve.[24]

[24] Ellis, Phys. Rev. **26**, 469 (1925).

This method of recording spectra has the disadvantage of not always indicating the relative intensities among the various bands. When the energy curve has a steep slope, a band of considerable intensity may be manifest only by a point of inflection in the absorption curve. Nevertheless, repeated records show that great reliance may be placed upon the details of such curves. Thus, numerous minor bands, of importance in identifying members of a series, especially in the region between 2μ and 3μ have been revealed. As an example, there is no doubt in the writer's mind but the two points of inflection in the spectrum of benzene occurring in Fig. 4 between 2.18μ and 2.52μ represent bands at approximately 2.32μ and 2.44μ. In toluene these have merged together into a broad band with maximum absorption at 2.38μ, yet the duplicity of this band is still apparent. In the higher homologues, the xylenes and mesitylene, this combination band has been so deepened as to partially include the one at 2.18μ.

If we assume a linear series of bands expressible by the formula,

$$\nu_n' \times 10^{-12} = An = 10.71n, \tag{4}$$

or

$$\lambda_n' = 28/n \tag{4'}$$

we seem to be able to trace the series to include about twenty-eight members, in the spectra of compounds of both the chain and the ring type. There are, however, numerous cases in which the bands become partially, or wholly, superposed upon members of the C-H series. In many cases, as heretofore explained, these are manifested by distinct points of inflection; while in other cases, although not capable of detection, these help to account for the abnormal depth of the C-H

TABLE II

Agreement between calculated wave-lengths of the C-H series and corresponding values observed in the spectra of various compounds.

	Calc. λ	benzene C_6H_6	toluene $C_6H_5CH_3$	p-xylene $C_6H_4(CH_3)_2$	mesitylene $C_6H_3(CH_3)_3$	pentane C_5H_{12}	hexane C_6H_{14}	heptane C_7H_{16}	octane C_8H_{18}
λ_1	6.44μ	6.8μ	6.85μ	6.85μ	6.85μ	†	6.86μ	†	6.87μ
λ_2	3.28	3.25	3.45	3.45	3.45	†	3.43	†	3.43
λ_3	2.22	2.18*	2.19*	2.20**	2.20**	**	**		**
λ_4	1.695	1.66*	1.70*	1.705*	1.70*	1.705*	1.72*	1.72*	1.72*
λ_5	1.38	1.39*	1.375*	1.38*	1.37*	1.375*	1.38*	1.38*	1.385*
λ_6	1.172	1.145*	1.155*	1.155	1.18*	1.185*	1.195*	1.19*	1.195*
λ_7	1.022	1.03*	1.025*	1.02*	1.015*	1.015*	1.03*	1.035*	1.035*
λ_8	0.912	0.885	0.915	0.915*	0.915	0.915	0.925	0.925	0.930
λ_9	0.826	†	†	†	0.825	†	†	0.835	†
λ_{10}	0.758	†	†	†	0.750	†	†	0.765	†

* Has another band superposed upon it.
** Occurs as a point of inflection only.
† No measurements recorded.

band. A good example of the latter occurs near 1.18μ, in which region the twenty-third, twenty-fourth and twenty-fifth members of the series of formula (4) become superposed upon the sixth member of the C-H series. It has also been stated that such superpositions cause an apparent shift of members of the C-H series to slightly different wave-length positions; but there are doubtless real shifts in the positions of these bands as well. However, the molecule as a whole has a surprisingly small effect upon these spectra. The agreement of the observed wave-length values of the C-H bands of a number of substances of the two types mentioned above with the values calculated from formula (1) is shown in Table II.

Table III shows the agreement between the observed bands attributed to a C-C series in the spectra of benzene and its simple methyl derivatives and their corresponding members calculated from formula (4). Table IV gives a similar agreement in the case of liquids of the paraffin series.

TABLE III

Calculated and observed wave-lengths in a C-C series for benzene and its homologues.

	Calc. $\nu' \times 10^{12}$	Calc. λ	benzene C_6H_6	toluene $C_6H_5(CH_3)$	o-xylene $C_6H_4(CH_3)_2$	m-xylene $C_6H_4(CH_3)_2$	p-xylene $C_6H_4(CH_3)_2$	mesitylene $C_6H_3(CH_3)_3$
λ'_1	10.7	28.0μ	##	##	##	##	##	##
λ'_2	21.4	14.0	14.1μ	13.85μ	13.55μ	12.95μ	12.55μ	11.95μ
λ'_3	32.1	9.35	*	9.3		9.2	9.0, 9.6	9.65
λ'_4	42.8	7.00	**	7.3**	7.3**	7.3**	7.3**	7.3**
λ'_5	53.5	5.60	5.5	5.5	5.35	5.35	5.4	5.5
λ'_6	64.2	4.67						
λ'_7	74.9	4.00						
λ'_8	85.6	3.50	*	*	*	*	*	*
λ'_9	96.3	3.11	*	*	*	*	*	*
λ'_{10}	107.1	2.80	2.8	2.8	2.82		2.78	2.8
λ'_{11}	117.8	2.545	2.52	2.53	2.54	2.52	2.52	2.54
λ'_{12}	128.5	2.33	2.32	2.32**	2.33**	2.33**	2.33**	2.33**
λ'_{13}	139.2	2.15	2.18*	2.19*	2.20*	2.20*	2.20**	2.20**
λ'_{14}	149.9	2.00	2.05*	2.03*	2.0*	2.0*	2.03*	2.02*
λ'_{15}	160.6	1.865	1.855	1.86	1.86	1.86	1.86	1.86
λ'_{16}	171.3	1.75	1.74	1.70*	1.75**	1.75**	1.75	1.75
λ'_{17}	182.0	1.645	1.66*	1.70*	1.64**	1.64**	1.705*	1.70*
λ'_{18}	192.7	1.555			**	**		
λ'_{19}	203.4	1.475	1.47	1.475**	1.46**	1.46**	1.47**	1.47**
λ'_{20}	214.0	1.400	1.39*	1.375*	1.40**	1.40**	1.38*	1.37*
λ'_{21}	224.8	1.335	1.33*	1.375*	1.33**	1.33**	1.38*	1.37*
λ'_{22}	235.6	1.270						
λ'_{23}	246.3	1.215	**	**	1.21**	1.21**	1.195	1.18*
λ'_{24}	257.0	1.165	1.145*	1.155*	1.17**	1.17**	1.155*	1.18*
λ'_{25}	267.8	1.120	1.145*	1.155*	1.11**	1.11**	1.155*	1.18*
λ'_{26}	278.5	1.075			1.06**	1.06**		
λ'_{27}	289.3	1.035	1.03*	1.025*	1.03**	1.03**	1.02*	1.015*
λ'_{28}	300.0	1.000	1.03*	1.025*	1.0	1.0	1.02*	1.015*

* Superposed upon another band.
** Occurs as a point of inflection only.
Region never investigated.

In these tables the values for the second, third, fourth and fifth members are taken from Coblentz's data, the values for the tenth to the thirteenth members inclusive from the records of the present investigation, while those for the last fifteen members, with the exception of ortho- and

TABLE IV

Calculated and observed wave-lengths in a C-C series for paraffin compounds.

	Calc. $\nu' \times 10^{-12}$	Calc. λ	pentane C_5H_{12}	hexane C_6H_{14}	heptane C_7H_{16}	octane C_8H_{18}	decane $C_{10}H_{22}$
λ'_1	10.7	28.0μ	††	††	††	††	††
λ'_2	21.4	14.0	†	13.9	†	13.83	†
λ'_3	32.1	9.35	†	9.4	†	9.3	†
λ'_4	42.8	7.00	†	7.35	†	7.35	†
λ'_5	53.5	5.60	†	5.8	†	5.75	†
λ'_6	64.2	4.67	†		†		†
λ'_7	74.9	4.00	†		†		†
λ'_8	85.6	3.50	†	*	†	*	†
λ'_9	96.3	3.11	†	*	†	*	†
λ'_{10}	107.1	2.80	2.8	2.8	†	2.8	2.8
λ'_{11}	117.8	2.545	2.5*	2.5*	†	2.5*	2.5*
λ'_{12}	128.5	2.33	2.33**	2.33**	†	2.33**	2.33**
λ'_{13}	139.2	2.15	**	**	†	**	**
λ'_{14}	149.9	2.00	2.02	2.02	2.0	2.0	2.0*
λ'_{15}	160.6	1.865	1.83	1.83	1.83	1.83	1.90*
λ'_{16}	171.3	1.75	1.75*	1.75*	1.75*	1.75*	1.73*
λ'_{17}	182.0	1.645	1.705*	1.72*	1.72*	1.72*	1.64**
λ'_{18}	192.7	1.555					**
λ'_{19}	203.4	1.475	**	**	**	**	1.47**
λ'_{20}	214.0	1.400	1.38*	1.38*	1.38*	1.385*	1.40**
λ'_{21}	224.8	1.335	1.38*	1.38*	1.38*	1.385*	1.34**
λ'_{22}	235.6	1.270					
λ'_{23}	246.3	1.215	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{24}	257.0	1.165	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{25}	267.8	1.120	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{26}	278.5	1.075					1.08
λ'_{27}	289.3	1.035	1.015*	1.035*	1.035*	1.035*	1.03*
λ'_{28}	300.0	1.000	1.015*	1.035*	1.035*	1.035*	1.0

* Superposed upon another band.
** Occurs as a point of inflection only.
† No measurements recorded.
†† Region never investigated.

meta-xylene and decane, are taken from the writer's curves previously published. The short wave-length values for ortho-and meta-xylene and decane are taken from the new curves of this investigation recorded in Fig. 6.

It has been pointed out that extrapolation of the C-H series indicates that the first member should occur at 6.44μ. The mean value actually observed by Coblentz for these compounds is about 6.85μ, giving a discrepancy of about +0.4μ. There is a discrepancy of +0.3μ between the observed and calculated values for the fourth member of the C-C series at 7μ. Furthermore, in the case of the open chain compounds there seems to be a corresponding error of about 0.2μ in the fifth member

at 5.8μ. These errors, if real, indicate a progressive error in the positions of bands between 3μ and 8μ which reaches a maximum value between 6μ and 7μ and which disappears beyond 9μ. If this error exists, it is doubtless due to inaccurate values of the refractive indices of rock-salt rather than to experimental errors, since measurements by various investigators are fairly consistent in this region. The writer is cognizant of the fact, however, that these indices have been determined by investigators skillful in the technique of infra-red spectroscopy.

There seems to be no detectable deviation from linearity in the case of this latter series, although according to Kratzer the members of the

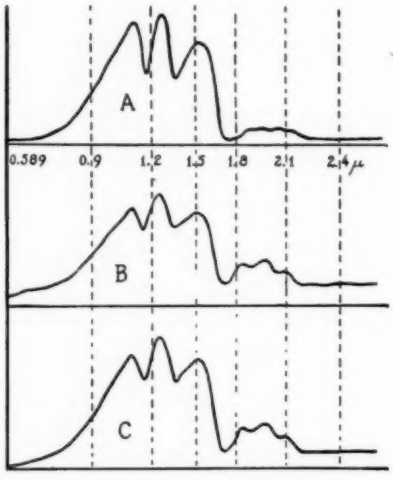

Fig. 6. Absorption spectra obtained with a registering quartz spectrograph.
A—8mm decane
B—8mm o-xylene
C—8mm m-xylene

series originate from a cause which should also cause them to depart from a true multiple relationship, namely, the non-harmonic motion of the bonded atoms arising from the non-linearity in the law of force acting. However, in the case of the C-C pair we have a symmetry which is lacking in the C-H group. There probably is a greater amplitude of vibration in the latter case because of the relative lightness of the hydrogen atom, and hence we should expect a greater departure from true harmonic motion than occurs in the oscillations of a C-C pair.

Combination Frequencies

Kratzer's theory is built upon a quantum theory basis, the absorption frequencies arising from successive integral changes in the rates of

TABLE V

Combination bands of C-H and C-C series.

	calc. $\nu\times10^{-12}$	calc. λ	benzene	toluene	o-xylene	m-xylene	p-xylene
$\nu_1+\nu'_1$	57.2	5.23	**	5.2	5.35*	5.35*	5.35*
$\nu_1+\nu'_2$	68.2	4.40	4.4				
$\nu_1+\nu'_3$	78.7	3.81	*	*	*	*	*
$\nu_1+\nu'_4$	89.5	3.35	*	*	*	*	*
$\nu_1+\nu'_5$	100.0	3.00	*	*	*	*	*
$\nu_1+\nu'_6$	110.5	2.71	2.75	2.72	2.72	2.72	2.72
$\nu_1+\nu'_7$	122.0	2.46	2.44*	2.38*	2.37*	2.37*	2.37*
$\nu_1+\nu'_8$	132.0	2.27	2.18*	2.19*	2.20*	2.20*	2.20*
$\nu_2+\nu'_1$	102.5	2.93					
$\nu_2+\nu'_2$	113.0	2.65		2.66	2.63	2.63	2.63
$\nu_2+\nu'_3$	124.0	2.42	2.44*	2.38*	2.37*	2.37*	2.37*
$\nu_2+\nu'_4$	134.5	2.23	2.18*	2.19*	2.20*	2.20*	2.20*
$\nu_2+\nu'_5$	145.0	2.07	2.05*	2.03*	2.05*	2.05	2.03*
$\nu_2+\nu'_6$	156.0	1.925	1.89	1.86*	1.86*	1.86*	1.86*
$\nu_3+\nu'_1$	145.5	2.06	2.05*	2.03*	2.05*	2.05*	2.03*
$\nu_3+\nu'_2$	156.5	1.915	1.89*	1.86*	1.86*	1.86*	1.86*
$\nu_3+\nu'_3$	167.0	1.795	1.79*	1.70**	1.86*	1.86*	1.70*
$\nu_3+\nu'_4$	178.0	1.685	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_3+\nu'_5$	188.5	1.59	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_4+\nu'_1$	187.5	1.60	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_4+\nu'_2$	198.5	1.51					
$\nu_4+\nu'_3$	209.0	1.435	1.39*	1.375*	**	**	1.38*
$\nu_4+\nu'_4$	219.5	1.365	1.39*	1.375*	1.36*	1.36*	1.38*

Combination bands of C-H and C-C series.

	calc. $\nu\times10^{-12}$	calc. λ	mesitylene	pentane	hexane	octane	decane
$\nu_1+\nu'_1$	57.2	5.23	5.35*	♯			♯
$\nu_1+\nu'_2$	68.2	4.40	**	♯	**		♯
$\nu_1+\nu'_3$	78.7	3.81	*	♯	*	*	♯
$\nu_1+\nu'_4$	89.5	3.35	*	♯	*	*	♯
$\nu_1+\nu'_5$	100.0	3.00	*	♯	*	*	♯
$\nu_1+\nu'_6$	110.5	2.71	2.72	2.72	2.72	2.72	2.72
$\nu_1+\nu'_7$	122.0	2.46	2.36*	2.38*	2.38*	2.38*	2.38*
$\nu_1+\nu'_8$	132.0	2.27	2.20*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_1$	102.5	2.93					
$\nu_2+\nu'_2$	113.0	2.65	2.63	2.65	2.65	2.65	2.65
$\nu_2+\nu'_3$	124.0	2.42	2.36*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_4$	134.5	2.23	2.20*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_5$	145.0	2.07	2.02*	2.0*	2.0*	2.0*	2.08*
$\nu_2+\nu'_6$	156.0	1.925	1.86*	1.9*	1.9*	1.9*	1.90*
$\nu_3+\nu'_1$	145.5	2.06	2.02*	2.0*	2.0*	2.0*	2.08*
$\nu_3+\nu'_2$	156.5	1.915	1.86*	1.9*	1.9*	1.9*	1.90*
$\nu_3+\nu'_3$	167.0	1.795	1.70*	1.75*	1.75*	1.75*	1.80
$\nu_3+\nu'_4$	178.0	1.685	1.70*	1.705*	1.72*	1.72*	1.72*
$\nu_3+\nu'_5$	188.5	1.59	1.70*	1.60*	1.72*	1.72*	**
$\nu_4+\nu'_1$	187.5	1.60	1.70*	1.60*	1.72*	1.72*	**
$\nu_4+\nu'_2$	198.5	1.51					
$\nu_4+\nu'_3$	209.0	1.435	1.37*	1.375*	1.38*	1.385*	**
$\nu_4+\nu'_4$	219.5	1.365	1.37*	1.375*	1.38*	1.38*	1.37*

* Superposed upon another band.
** Occurs as a point of inflection only.
♯ No measurements recorded.

vibration within the molecule. It would seem probable that if a carbon atom is bonded both to a hydrogen and another carbon atom that a new frequency ν_c would be absorbed provided that

$$\nu_c = \nu_m + \nu_n' \tag{5}$$

where ν_m and ν_n' are low frequency members of the C-H and C-C series respectively. This means that a quantum of energy would be divided between the two absorbing centers.

Table V shows the new absorption frequencies to which such a phenomenon would give rise, and an attempted identification of their corresponding wave-lengths with bands actually observed in the curves of Figs. 1-6. The two series, with these simple combinations, seem to satisfactorily account for practically all of the bands, up to about 7μ, observed in the spectra of the simple hydrocarbons. In no case do these series demand a band of major intensity which cannot be accounted for. The bands predicted by formulae (4) and (5) between 3.5μ and 5.5μ do not appear in the ordinary spectra, probably because of the unusually low dispersion of rock salt in this region and the thinness of absorption cell used. In the instances where Coblentz used a large spectrometer, of greater resolution, many of these bands appeared. Their values have been included in Tables III, IV and V. The numerous bands occurring more or less regularly between 8μ and 15μ, for all substances, and the rather prominent band at 6.2μ in the spectrum of benzene and its derivatives, are not accounted for by such series.

It also seems that the conditions would be appropriate for a division of an energy quantum between two C-H groups sharing the same carbon atom. This would cause the second member of the C-H series to appear with unusual intensity. This phenomenon is observed, especially in the spectra of the paraffin compounds, as may be seen in Fig. 2.

Methane, CH_4, should have a very simple spectrum, since it has only bonds of the C-H type. Coblentz's curve shows it to have but three absorption bands, at 7.7μ, 3.31μ and 2.35, which may be identified as the first three members of the C-H series, in spite of the shift of the first member toward longer wave-lengths. In the spectrum of ethane, C_2H_6, these three bands appear, with the first member in the position which it occupies in the spectra of the higher liquid members of the paraffin series to which this gas belongs. It is impossible to identify any members of a C-C series, although there is an undefined group of bands at 12μ. In the spectrum of butane, C_4H_{10}, we have the three C-H bands as in ethane, and in addition there are bands at 14μ and

5.65μ which may be identified as the second and fifth members respectively of a C-C series.

In the spectra of the ring compounds there is a considerable variation in the position of the 14μ band. This band shifts progressively toward a shorter wave-length value with successive substitutions of a methyl group, CH_3. In the spectra of the xylenes, $C_6H_4 \cdot (CH_3)_2$, the position of this band also depends upon the positions of such substituted groups. Table VI shows the displacements of this band. Its average value for all the compounds examined by Coblentz is about 13.7μ. The shorter wave-length spectra of the compounds of Table VI are quite similar.

TABLE VI

Displacement of the 14 μ band in the spectra of the benzene derivatives.

benzene	14.1μ
toluene	13.85
o-xylene	13.55
m-xylene	12.95
p-xylene	12.55
mesitylene	11.95

If C-C and C-H pairs of atoms give rise to linear, or approximately linear, series of absorption bands, then we should expect other bonded pairs within the molecule to behave in a similar manner. In a later paper it will be shown that the shorter wave-length bands occurring in addition to the members of the C-H series in the spectra of simple halogen derivatives of the benzene and paraffin series can be accounted for on the basis of carbon-halogen series starting near 17μ, and combinations between such series and the carbon-hydrogen series.

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CHANGES IN THE REFRACTIVE INDEX OF HELIUM PRODUCED BY A GLOW DISCHARGE

By W. H. McCurdy* and A. Bramley

Abstract

Interferometer method of measuring the concentration of ions and excited atoms in a glow discharge.—According to the Lorentz theory, the presence of atoms in a state s should change the index of refraction of the discharge for light of wave-length $(\lambda=\lambda_s+\delta\lambda_s)$ by an amount $\delta n=(N_s e^2/8\pi^2 c^2 m)(\lambda^3_s/\delta\lambda_s)$, where N_s is the concentration of excited atoms. Kramer's theory leads to a somewhat different relation. To measure δn, a Michelson interferometer was used into one arm of which was introduced a cylindrical discharge tube with a filament cathode in a side arm, and a ring anode, so that the light passed along the positive column. In the tests made with He, an iron arc was used as source, and the light from the half silvered mirror was focussed on the slit of a spectrograph. When the glow discharge was started (30 to 40 m-amp.), shifts to .2 to .5 fringe were observed for about 15 Fe lines. In each case the shift was positive or negative according as the wave-length was greater or less than that of a neighboring He line. The results are not quantitative as yet but prove the practicability of the method.

PREVIOUS methods of determining the concentration of ions in gaseous discharges[1] may introduce electrical disturbances arising from the presence of exploring electrodes which, in some cases, cause doubt about the accuracy of the results. Furthermore, these methods are powerless to detect or to measure the concentration of excited atoms or molecules, which often play an important rôle.[2] For these reasons the following optical method has been devised to measure these concentrations and the preliminary tests prove it to be capable of practical application. The method is based on measurement of the refractivity of the gas in the spectral region close to emission or absorption lines in its spectrum, and the interpretation of these measurements by current theories of optical dispersion. The possibility of making such measurements was demonstrated by Ladenburg and Loria.[3]

The apparatus (Fig. 1) consisted of a discharge tube 6 inches (15.2 cm) long, placed in one arm of a Michelson interferometer. The tube

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[1] Langmuir and Mott-Smith, Gen. Elec. Rev. **26**, p. 731 (1923); **27**, pp. 444-538 (1924).

[2] Compton, Turner and McCurdy, Phys. Rev. **24**, p. 597 (1924).

[3] Ladenburg and Loria, Verh. d. D. Phys. Ges. **10**, p. 858 (1908).

itself was made with a hot cathode F in a side tube and a ring anode A through which the light could pass, and with the two optical glass end plates cemented to the ground ends of the tube. By this arrangement the part of the discharge in the arm of the interferometer included only the positive column, which contains the highest concentration of excited atoms.

The success of the experiment depended upon the use of light of practically the same wave-length as that of a line in the spectrum of the positive column. A strong iron arc S was used as the source of light for the interferometer. The light, after passing through the interferometer, was bent to a convenient direction by a right angle prism P and focussed by a system of lenses on the slit I of a monochromatic illuminator of

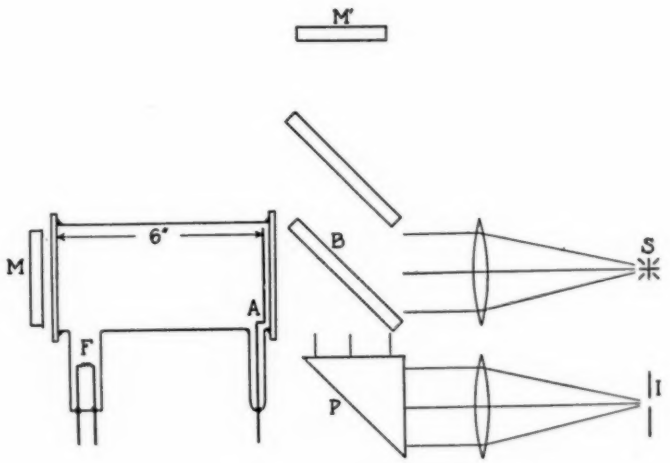

Fig. 1. Diagram of apparatus.

good resolving power. The fringes were then observed by means of a telescope after the light had been resolved by the illuminator. In order to measure the amount of shifting of the fringe system on starting or stoping the discharge, the telescope was replaced by a camera with an equivalent lens system. The displacement of the fringe system due to the change in refractive index on starting the discharge, was recorded with the camera by taking three adjacent exposures, the two outside being with no discharge while the center one was taken with the discharge running. This gave a convenient method of determining the fraction part of a fringe separation by which the system had been moved by the action of the discharge.

As this method depends on measuring the change in the refractive index of the gas with regard to a certain line when the discharge is

started, we will next consider the various formulas which connect the index of refraction with the concentration of atoms in the various states. According to Lorentz's formula, the index of refraction n is connected with the wave-length λ of the light used and concentration N and natural wave-length λ_s of the atoms in the s state by the relation

$$n^2-1=\frac{e^2}{4\pi^2c^2m}\ \frac{N_s\lambda_s^4}{(\lambda^2-\lambda_s^2)}+\text{const.}, \tag{1}$$

if λ_s differs from λ by a small quantity. Taking the case of normal incidence of light on the mirrors, the condition for a fringe (darkness) at a given position is

$$2dn=p\lambda$$

where p is an integer and d is the difference of the distances of the two mirrors M and M' from the half-silvered mirror B. Thus the change in n corresponding to a fractional shift f is

$$\delta n=(\lambda/2l)f \tag{2}$$

where l is the length of the tube. Letting $\lambda=\lambda_s+\delta\lambda_s$ we find for N_s in terms of f, λ_s and $\delta\lambda_s$ the expression

$$N_s=\frac{4\pi^2c^2m}{e^2l}\ \frac{\delta\lambda_s}{\lambda_s}\qquad =10\frac{\delta\lambda_s}{\lambda_s^2}f \tag{3}$$

where $\delta\lambda_s$ is measured in angstroms and λ_s in microns.

According to Kramers,[4] if the atom is in a state s which absorbs energy of frequency $\overset{a}{\nu}_{s_1}\cdots\overset{a}{\nu}_{s_n}$ and emits energy of frequency $\overset{e}{\nu}_{s_1}\cdots\overset{e}{\nu}_{s_n}$ under the influence of external radiation, while $\overset{a}{A}_{s_1}\cdots\overset{a}{A}_{s_n}$ and $\overset{e}{A}_{s_1}\cdots\overset{e}{A}_{s_n}$ represent the probabilities of a transition from the state s to a lower or higher energy level with the emission or absorption of energy respectively, and if N is the total number of atoms and $\overset{a}{\tau}_{s_i}$ and $\overset{e}{\tau}_{s_i}$ represent the life of the excited state s_i for the frequency $\overset{a}{\nu}_{s_i}$ and $\overset{e}{\nu}_{s_i}$, then

$$n^2-1=N\left[A_s{}^a\tau_s{}^a\frac{e^2}{4\pi^2c^2m}\ \frac{(\lambda_s{}^a)^4}{(\lambda^2-(\lambda_s{}^a)^2)}-A_s{}^e\tau_s{}^e\frac{e^2}{4\pi^2c^2m}\ \frac{(\lambda_s{}^e)^4}{(\lambda^2-(\lambda_s{}^e)^2)}\right]+\text{const.},$$

where $\lambda_s{}^a$ and $\lambda_s{}^e$ lie near λ. Since the above type of apparatus measures only the change in refractive index in the neighborhood of a particular line, the frequency $\lambda_s{}^a$ must equal $\lambda_s{}^e$ and Kramer's equation becomes

[4] Kramers, Nature, May 10, 1924, p. 273 and Aug. 30, 1924, p. 310.

$$n^2-1=\frac{e^2N}{4\pi^2c^2m}\left[A_s^a\tau_s^a-A_s^e\tau_s^e\right]\frac{\lambda_s^4}{(\lambda^2-\lambda_s^2)}+\text{ const.}$$

The quantity $N[A_s^a\tau_s^a-A_s^e\tau_s^e]$ which replaces the concentration N_s of Lorentz's classical formula, represents the average increase per unit time in the number of atoms in the state s due to the absorption and emission of light of frequency ν_s.

In the following table are given the observed fringe shifts for the various excited states of He, investigated in the visible and violet region of the spectrum by this method. The intensity of the lines are given in the bracket, while the shifts are given as fractions of one fringe spacing. In addition to these, shifts with about eight other lines were observed

TABLE 1

Current in tube	State	He line	Fe line	Shift
30 m-amp	$1P-3D$	4921.929 (4)	4920.52 (6)	−.4 fringe
30	$1P-4D$	4387.928 (3)	4383.55 (10)	−.3
40	$1P-4D$	4387.928 (3)	4404.	.18*
40	$1P-5D$	4143.77 (2)	4143.88 (6)	−.5†
			4143.43 (6)	
35	$1P-2S$	5047.736 (2)	5049.8 (5)	−.12

visually, but not measured. In all cases the shift was positive or negative, according as the light was of wave-length greater or less than that of the neighboring helium line. As no shift could be observed for the lines which were 30 or 40 Angstroms from the nearest line of the helium spectrum, the temperature change on starting the discharge must have been negligible.

These results prove the practicability of the method and the possibility, with refinements and added data, of testing the existence of negative terms postulated in Kramer's dispersion formula and of using refractivity to measure the distribution of atoms in excited states in a discharge. This further work is now being carried on by one of us (W. H. Mc.).

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
October 14, 1925.

* This shift appears to be too large. The observed effect is probably in error.

† This shift might have been either + or − in sign as it was impossible to tell from the photographs in which direction the shift had occurred without taking visual observations.

COMPLEX MAGNETIZATION

By Eugene Peterson

Abstract

Magnetization of silicon steel by two sinusoidal fields of differing frequencies.—*The energy loss per cycle W* and the *flux density B* associated with each of the two frequencies were determined when the two sinusoidal magnetizing forces were simultaneously impressed on a toroidal silicon steel core built up of one-mil laminations. A null method was used which permitted suppression of the modulated currents and constancy of the impressed currents during manipulation for balance. The frequencies used were 400, 821 and 1582. Six sets of measurements were taken with fixed magnetizing forces ranging from 0.5 to 10 gilberts/cm and superposed forces up to 15 gilberts/cm. The results show that the effect of superposition depends upon the relative amplitudes and upon the frequency ratio R of the superposed frequency to the other. At low fixed fields W and B go through maxima as the superposed field is increased, the maximum value increasing with R. The maximum is less pronounced or absent for the higher fixed fields. In general B is smaller with a low than with a high value of R other things being equal. The effect on W is not as sharply defined; in general the effect of superposition is more pronounced the higher the superposed frequency. The amplitude effect and frequency ratio effect are shown to be in general agreement with conclusions drawn from mathematical treatment of somewhat simplified cases and it is concluded that the effects are not inconsistent with purely hysteretic phenomena.

THE present investigation is concerned with the behavior of iron under the simultaneous influence of two sinusoidal magnetizing forces, particularly with reference to the distribution of flux and of energy loss between the two superposed frequencies. The problem has apparently received no consideration although numerous investigators have determined the effect of an alternating magnetizing force on the flux due to a constant or slowly varying magnetizing force,[1] and others have determined the flux and energy associated with a high frequency force at various points of a cycle of low frequency magnetization.[2]

Experimental Arrangement

Supression of modulation. The varying reaction of an iron core coil during a cycle of the impressed field gives rise to new frequencies which are the sum and difference of integral multiples of each of the two impressed frequencies such that the sum of the integers is odd. Two

[1] From Lord Rayleigh, Phil. Mag. 1887, to Spooner Phys. Rev. April 1925.

[2] Turner, Phys. Rev. **21**, 74 (1923).
Fondiller and Martin, J.A.I.E.E. 1921.

distinct effects are produced by the flow of these modulated currents; the problem is complicated in a manner which is unknown since the effect is precisely the one in question in the simplest possible case of two impressed frequencies, and further, the flow of modulated current must produce in general an effective resistance and reactance to the fundamental frequencies. It is certain then that an investigation of the properties of iron under the action of alternating forces must be carried out in the absence of modulated components in the magnetizing force.

The desired suppression may be approximated to a satisfactory degree through the use of networks as shown in Fig. 1A marked $f_1 f_2$, which have the properties that energy from the sources is transmitted to the coil with small attenuation, that a high impedance is offered to

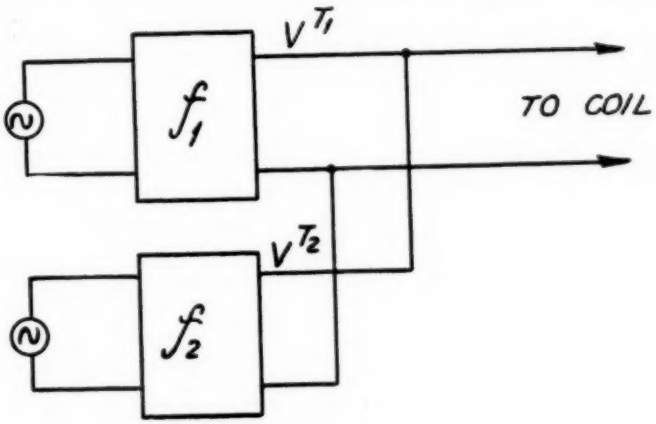

Fig. 1A

frequencies outside the transmitted range, and that the surge impedance of the networks is large compared to the coil impedance. This method also permits us to measure each of the two current components by inserting thermocouples and associated micro-ammeters at the points $T_1 T_2$ indicated in the figure.

Method of measurement, flux density and loss per cycle. The necessity for suppressing modulated components and the convenience of keeping the currents constant during a measurement led to the adoption of two methods,* one involving a Braun tube and the other involving an aural balance. The latter was used for the quantitative determination

* These conditions rule out the usual type of bridge. Suppression of modulated components may be effected in the bridge by inserting two large inductance coils having a high coupling coefficient in the two branches between which the generator current divides—and in one of which the iron-core coil is placed. The second condition is then unsatisfied however.

since it is capable of greater precision than the first; the first, however, enables one to explore the field in qualitative fashion (visually) in a comparatively short time; we may dispose of it with the statement that it depends upon the integration of the voltage due to the flux change by a condenser, and that desired components are selected by tuned circuits, amplified without distortion, and impressed upon the Braun tube plates to give component *B-H* ellipses.

The following null-method, which was used for the quantitative determination, is based upon the balancing of two voltages proportional to the flux and to the magnetizing force respectively. The particular arrangement used is shown in Fig. 1B, and involves the variation of capacity C and resistance r to attain balance, the other quantities R_0, r_1, R_φ and C_φ being fairly well fixed.

The two potentials to be balanced are taken from R_0 and C_φ respectively, and phase and amplitude adjustments are effected through r_1, r, and C which are connected in series across R_0. The potential across

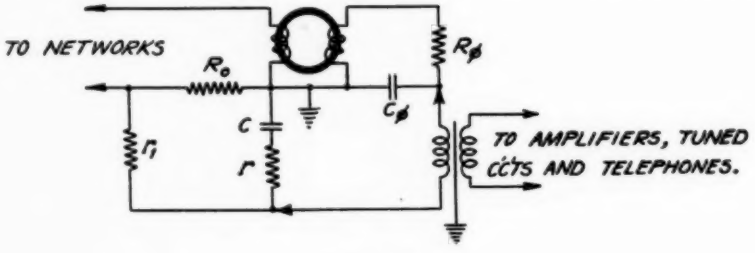

Fig. 1B

C_0 is taken from a closely coupled secondary through a relatively high resistance in order that the secondary may have inappreciable reaction upon the primary, as well as to have the measurements independent of the primary winding resistance. R_0 is made small compared to r_1 to keep the primary currents unchanged throughout the manipulation for balance; if it were otherwise the observations at definite currents would involve successive approximations or the equivalent.

A succession of amplifiers and tuned circuits is used to provide a sensitive indication of the balance point in connection with telephone receivers. The first stage of the amplifier is made to have a large load capacity so that modulation may not take place in the amplifier itself, since the balancing of the two voltages refers simply to a single frequency, and the tuned circuits are used to eliminate disturbing components produced by the coil which would otherwise obscure the null point since there are always, in general, modulated components near the fundamentals.

At the null point it may be shown that the flux linking with the secondary is given by

$$B=\frac{C_\varphi R_0 I}{n\sigma}10^8\left(\frac{(R_\varphi^2+1/p^2C_\varphi^2)(r^2+1/p^2C^2)}{(R_0+r+r_1)^2+1/p^2C^2}\right)^{\frac{1}{2}}$$

where n is the number of turns of wire on the secondary, σ is the core cross-section and I is the primary current, and that the phase angle of B referred to H is given by

$$\theta=\cot^{-1} pC(R_0+r+r_1) -\cot^{-1}pCr-\cot^{-1}pC_\varphi R_\varphi.$$

The energy loss in ergs per cycle per cc of core material is given by

$$4W_k=\Sigma B_k H_k \sin\theta_k$$

in which k refers to the component.

Instability of current[3] with applied e.m.f. is avoided by making the ratio of resistance to reactance of the circuit large, as may be shown analytically by application of the method of perturbations[4] to a simple B-H characteristic, and this condition works in the same direction as the condition for the suppression of modulated components.

Connections and apparatus were shielded and spaced inasmuch as high potentials were developed in the networks which would otherwise induce potentials in the sensitive amplifiers used to indicate balance and so lead to a false null-point. Further, shielded transformers were used at appropriate points to reduce capacitive coupling between the two sides of the shield. As a result of these precautions the currents at the highest frequency employed (1582 cycles) were found to be the same within one-third percent (within the error of observation) in the two wires leading to the coil, and the amplifier was found to have no potentials induced when the input terminals were short-circuited.

The frequencies chosen for the work were 400, 821 and 1582 cycles so that there were available frequency ratios of 3.95, 2.05, 1.93 and their reciprocals, made non-integral to avoid effects due to the relative phase of the two inputs, and adjusted to avoid formation of comparatively low impedance paths to the modulated products* of low order. These frequencies were used in pairs during the experiments and were supplied by vacuum tube oscillators and amplifiers, the frequency and amplitude being quite stable.

[3] Martienssen, Phys. Zeit., **11**, 448, (1910).

[4] Analogous to Appleton's treatment af the vibration galvanometer. Phil. Mag. **47**, 609 (1924).

*The last effect may be avoide l in this case by using the bridge arrangement mentione.l in the previous note.

The specimen. The core was built up of 17 rings of one mil (.025 mm) silicon steel having an inside diameter of one-half inch (1.27 cm) and a radial thickness of one-sixteenth inch, the weight being 0.237 gr and the cross-section .0070 cm^2. The winding consisted of two sections of 750 turns each uniformly distributed about the core and arranged to produce no cross-magnetization, by having alternate layers wound with a negative pitch. The coupling coefficient was measured at a low force and found to be 0.99; the turns ratio was found by reversing the windings to be 1.02, so that the data presented are to be increased by one percent. The resonant frequency of the coil under test was found to be of the order of 50,000 cycles so that resonant effects in the windings have negligible effect on the measurements.

Experimental Procedure

Six sets of measurements were taken over the range of magnetizing forces from 0.5 to 10.0 gilberts/cm r.m.s. so as to include regions on both sides of the maximum a.c. permeability which is found at about 2.5 gilberts/cm. The procedure followed during the measurements was to have the output of the oscillator supplying the measured frequency maintained constant so as to give 0.5, 1.4, 2.5, 4.4, 7.0, and 10 gilberts/cm in turn, and with the tuned circuits adjusted, to balance at a number of values of superposed current for each of the six frequency combinations.

In this sort of work the balance point drifts with time and depends upon the previous magnetic history. To make matters definite, therefore, a fairly large magnetizing force was applied for a few minutes before each run and the measurements proceeded from large fields down to small ones. It was usually found possible to check the results at different times to within five percent, although the settings were made usually to three or four places. The precision of adjustment was thus greater than the stability of the iron.

Experimental Results

Flux Density. For clearness in presenting the results we have plotted the flux densities (Fig. 2) and energy losses per cc per cycle (Fig. 3) separately and, of the six constant fields H' at which the amplitude and frequency of the superposed field H were varied, three of the more representative ones have been plotted, corresponding to the fields H' 0.5, 2.5, and 7.0 gilberts/cm. The difference in the six curves plotted for any one value of H' proceeds simply from the different frequency ratios involved. Flux densities and magnetizing forces are specified by r.m.s. values and the energy loss per cc per cycle is given in ergs.[1]

[1] The ordinates of Figs. 2, 3 are to be multiplied by 1000.

Thus to consider flux densities first we have at $H'=0.5$ a group of which the topmost curve represents the effect on the B at 400 cycles of a superposed H at 1582 cycles, which for convenience may be designated as the B_4-H_{16} characteristic. B increases by a factor of over four as H_{16} increases to 1.6 and then decreases at a slower rate. The next lower curves representing B_4-H_{16} and B_4-H_8, are almost coincident and reach maxima slightly less than four times the initial flux density. The curves B_8-H_4, B_{16}-H_8, B_{16}-H_4, reach maxima of about 2.5 times the initial and are almost coincident. To sum up, the effect of a superposed force at $H'=0.5$ is to cause the flux, or,what is the same thing, the per-

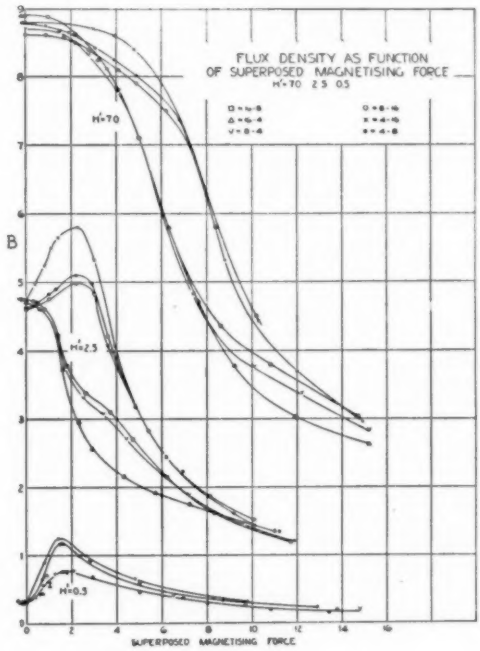

Fig. 2

meability to pass through a maximum, the magnitude of the maximum being greater for the lower frequency than for the higher. At large superposed fields all characteristic curves tend to coincide.

At an H' of 1.4 (not shown) the curves lie in the order of the frequency ratio. Superposition produces a smaller increase (a ratio of less than two in the case of B_4-H_{16}) than was the case of an H' of 0.5, but the B_{16}-H_4 characteristic diverges more than it did at the lower H and drops decidedly after passing through a slight maximum at a low H. Passing on to the second group for an H' of 2.5 at which the permeability is maximum, we find the increase due to superposition to be twenty-two

percent for B_4-H_{16} and about ten percent for B_4-H_8 or B_8-H_{16}. The maxima are found at larger superposed H's than was the case in the previous curves, and it seems that the superposed H required is slightly greater when the ratio of the superposed frequency to the original decreases. When the superposed H is made lower in frequency than the original, the curves pass through no maximum but decrease slowly at first and then rapidly, and seem to approach the H axis asymptotically. The curves again lie in the order of their frequency ratios.

The results obtained with fields of $H' = 4.4$, 7.0 and 10, of which only one ($H' = 7$) is plotted, are very similar and again the curves are found arranged according to frequency ratio.

We may summarize the effect of superposition upon flux density (or its equivalent in this case; permeability) by saying that with two impressed frequencies the flux of the low frequency is greater than that of the high frequency over the greater part of the characteristic so that the low frequency will pass through higher maxima, or the high frequency will start to decrease at lower superposed fields. There is apparently a further influence of the frequency ratio, such that a greater frequency ratio leads in general to a more pronounced effect and this is evidenced with frequency ratios differing by as little as six percent. This answers the question as to the partition of flux between the two frequencies impressed; the lower frequency has the greater flux density with equal fields of the two frequencies.

Energy Loss per Cycle. The determination of energy loss is somewhat less definite than that of flux since the variation with time appears to be somewhat greater. The results, with the same fields as those used for the flux density measurements, are shown in Fig. 3. The first group at $H' = 0.5$ exhibits a larger change (maximum ratio of 6.3, minimum of 3.2) with superposed H than did the flux, and the maxima are found in general at lower superposed H's. As with the flux the group of curves representing the effect of a higher superposed frequency lies above that representing a superposed frequency ratio of less than unity, considering the region near the maxima, but the curves are no longer ordered within each group corresponding to the frequency ratio. There also appears some tendency for the two groups to interchange relative positions at high fields. When the constant magnetizing force is maintained at 1.4 (not shown) the two frequency groups show the same effect but the change in energy loss is much reduced, as was true of the flux in similar circumstances. The curves are ordered according to the frequency ratio in the neighborhood of the maxima although they show a tendency to cross one another at higher fields. At $H' = 2.5$ the energy

peak is much reduced. The curves for superposed frequency ratio greater than unity pass through more pronounced maxima than the lower frequency ratio group, the two groups intersecting at large fields. The effect of eddy currents is apparent from the order of the curves at zero superposed H, the ordinates increasing with the measured frequency.

At $H' = 4.4$ (not shown) we find more pronounced maxima and greater rate of decrease for the higher ratio group. The results for $H' = 7$ and for $H' = 10$ (not shown) are quite similar bringing out the relations more

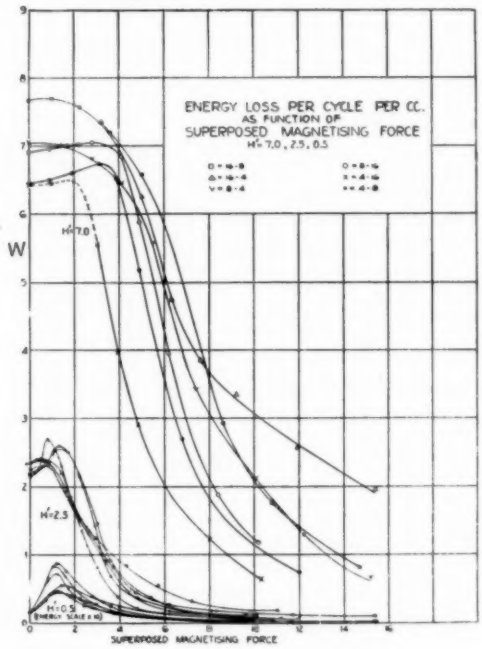

Fig. 3

clearly, and also showing a greater effect of eddy currents. It is only for ratios of superposed to measured frequency greater than unity that a maximum occurs, and these characteristics exhibit the greatest rate of decrease. Except for the effect of eddy currents, for which allowance may be made roughly from the initial values, the curves appear to be ordered as to frequency ratio.

We may summarize the results of the experiments on energy loss per cycle as follows: The maxima with high superposed frequencies are more pronounced and the decrease is more rapid beyond the maxima so that in general as we pass out to increased superposed fields we find the order of the characteristics inverted; the high superposed fre-

quency curves lie below the lower frequency ones. Thus the partition of energy loss between the two input frequencies depends decidedly upon the superposed field strength. These effects are somewhat masked by eddy current losses at high fields but the same conclusions may be made if we adjust the curves corresponding to the different frequencies to have the same initial energy loss. The maxima are found at all fields investigated when the superposed frequency is greater than that measured. The course of the phenomenon bears a general resemblance to that of flux density although the maxima occur at lower superposed fields.

It is easy to find regions in which the total energy loss under superposed conditions is less than the energy loss with a high frequency alone impressed; this corresponds to hysteresis suppression and appears to find a ready explanation in the shifting of the displaced high frequency loops to regions of small energy loss which exist along the more nearly saturated parts of the magnetization characteristic.

It may be stated that other magnetic materials, permalloy for example, show the same sort of effects due to superposition as those observed in silicon steel.

Discussion of Results

One question which arises upon inspection of the data is as to the cause of the frequency ratio effect there evidenced; a complete answer is of course impossible but it may at least be shown that the frequency ratio effect is not inconsistent with a hysteresis cycle, itself independent of the frequency or frequency ratio. The hysteresis loop used for the analysis is obtained from Honda and Okubo's extension[5] of Ewing's model which presents perhaps the least unsatisfactory picture of the course of the B-H loop. Fig. 4 represents a typical loop in which the equilibrium axis of a single complex is taken at 60° to the axis of the impressed magnetizing force; the full lines represent stable states and the dotted lines unstable states. Subsidiary loops are to be observed. The result is independent of the frequency of the applied force except in so far as temperature agitation may cause irreversible changes through shifting in effect the angle of the complex.

We now suppose a two-frequency magnetizing force to be impressed on a loop idealized by having the lines representing stable states parallel to the h-axis and by putting unstable states at convenient points. The two fundamental components may be calculated by the usual methods of Fourier analysis which are rather long in the cases considered

[5] Honda and Okubo, Tohoku Univ. Sci. Report **V**, 153 (1916).

despite the simplifications mentioned above. The results of the calculation are tabulated below:

Ratio of Measured to Superposed Frequency	Flux Density proportional to	Energy Loss per Cycle proportional to
1:5	9.65	8.25
1:3	8.36	6.15
3:1	6.71	5.94
5:1	4.56	3.99

and are observed to be ordered as to frequency ratio; we may conclude that the frequency-ratio effect is capable of production by purely hysteretic loops.

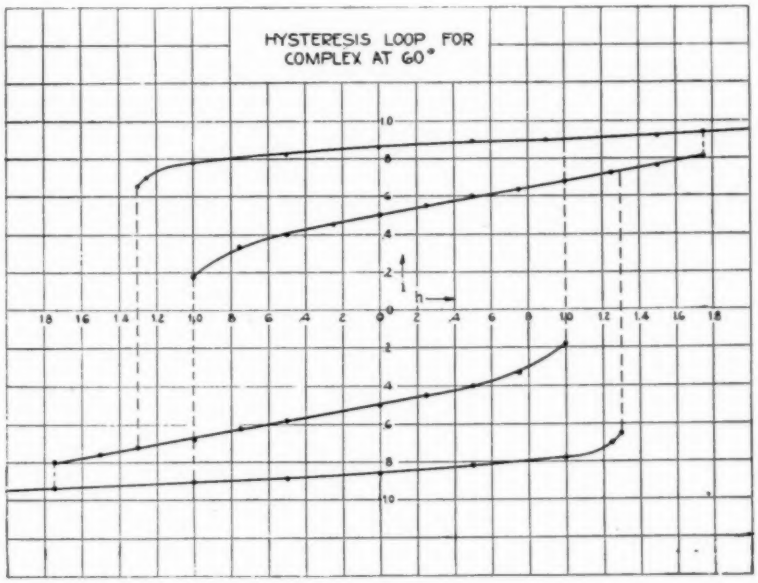

Fig. 4

The curves obtained experimentally in the case of a large ratio of the superposed to the measured frequency are similar to those obtained with a single constant impressed force plotted as a function of temperature in this respect, that the flux passes through a maximum at low fields and decreases progressively at high fields. A complex may possibly take up the increased energy due to heat in two ways; in changing the angle of the lattice considered as a whole—an organizing effect because of the irreversible changes mentioned above—and in changing the angles of the elementary magnets within the complex which would have a disorganizing effect. Apparently the first effect is preponderant with

small magnetizing forces and the second necessarily with large forces. The effect of a superposed magnetizing force differs from that of heat since the superposed force is applied substantially along a unique axis at a definite frequency.

It may be shown that in the case of a small high frequency and a large low frequency force, the high frequency permeability depends roughly upon the permeability to the low frequency field and that the low frequency flux is practically unaffected by the superposed high frequency, as is found experimentally. This is accomplished by expressing the hysteresis loop branches of a family of hysteresis loops by double power series and combining in a Fourier series for a complete cycle.

The writer acknowledges his obligation to Professor Wills and to Professor Webb of Columbia University for suggestions and encouragement.

BELL TELEPHONE LABORATORIES, INCORPORATED
November 18, 1925.

ASSOCIATION, ADSORPTION, AND DIELECTRIC CONSTANT

By C. T. Zahn

Abstract

Dielectric constant of water vapor at pressures 3 to 20 mm and at temperatures 23 to 165°C.—Using a heterodyne beat method previously described, a study has been made of the variation of the dielectric constant with pressure and temperature. At room temperature, the curve connecting $(\epsilon-1)$ with pressure consists of two straight parts connected by a transition curve. This change of slope is less marked at higher temperatures and disappears at about 47°C. The rectilinear portion below the transition pressure corresponds to the normal behavior of water vapor. The abnormal behavior above the transition pressure cannot be explained satisfactorily by the association theory suggested by Jona in connection with his results. It is suggested, rather, that the anomaly is due to the formation of an adsorbed layer of water on the condenser plates. As the number of adsorbed molecules increases, the vapor pressure increases, approaching the ordinary vapor pressure as a limit. The final thickness of the layer at saturation pressure is of the order of the radius of molecular attraction and comes out of the order of several microns, corresponding to about 200 molecular layers. The experimental results are in general agreement with this theory.

IN a recent series[1] of measurements of the dielectric constants of a number of dipole gases by the author, complete agreement with the Debye theory was obtained except for the possibility of very slight deviations in one or two cases. On the other hand experiments by Jona[2] showed marked anomalous increases of the dielectric constant near the liquefaction points of several vapors. SO_2 among others showed a considerable increase. More recent observations by the author did not show this effect. Jona attributed the effect to association of the molecules with an accompanying increase in the electric moment of the resulting molecule. On account of these apparent inconsistencies a more thorough investigation of this effect has been made both theoretically and experimentally.

Association and the Dielectric Constant

Debye's equation may be put in the form

$$(\epsilon-1)=N(a+b/T)$$

[1] C. T. Zahn, Phys. Rev. **4**, 400 (1924).
C. P. Smyth and C. T. Zahn, Journ. Amer. Chem. Soc. **47**, 2501 (1925).
And recent data on CO_2, NH_3, and SO_2 about to appear.

[2] M. Jona, Phys. Zeits. **20**, 14 (1919).

where ϵ is the dielectric constant, N the number of molecules per cubic centimeter, T the absolute temperature, a a constant representing the effect of molecular distortion, and b a constant proportional to the square of the molecular electric moment and representing the effect of molecular orientation. If the gas consists of a mixture of two kinds of molecules defined by N_1, a_1, b_1 and N_2, a_2, b_2 then

$$(\epsilon-1)=N_1a_1+N_2a_2+(N_1b_1+N_2b_2)/T$$

If these two types of molecules correspond to single and to double (associated) molecules and the law of additivity of refractivity be assumed; i.e., $a_2=2a_1$ then

$$\frac{\epsilon-1}{N_1+N_2}=(1+c_2)a_1+[1+(r-1)c_2]\frac{b_1}{T}$$

where $c_2=N_2/N_1+N_2$, the concentration of double molecules and $r=b_2/b_1=\mu_2^2/\mu_1^2$, the square of the ratio of the electric moments of the double and single molecules. As a first approximation it is assumed that the partial pressures of the two constituents can be determined from the ideal gas law which can be stated $p_1=TN_1/273N_0$ where N_0 is the number of gas molecules per cubic centimeter at 0°C and 760 mm Hg. Then

$$p=p_1+p_2=\frac{T}{273N_0}(N_1+N_2)$$

or

$$N_1+N_2=273N_0p/T$$

and the modified Debye equation becomes

$$\frac{(\epsilon-1)T}{273N_0p}=(1+c_2)a_1+[1+(r-1)c_2]\frac{b_1}{T}$$

or

$$\frac{(\epsilon-1)T^2}{273N_0p}=(1+c_2)a_1T+[1+(r-1)c_2]b_1.$$

The concentration c_2 should be determinable from the thermodynamical consideration of equilibrium as Jona[2] has pointed out. According to Planck's[3] expression for chemical equilibrium in gaseous systems

$$c_1^{\nu_1}c_2^{\nu_2}\cdots=Ae^{-B/T}T^Cp^{-r}$$

or for the simple case of association

$$\frac{c_1^2}{c_2}Ae^{-B/T}T^Cp\,.$$

[3] Planck, Thermodynamik, 4 Aufl., 1913, § 241, p. 222.

It should be noted here that there is apparently a misprint in Planck's fourth edition at the top of page 223. The statement is made that the conservation of molecular heats requires that $\Sigma\nu_1 C_{p_1}=0$. The correct statement should be $\Sigma\nu_1 C_{v_1}=0$ which is equivalent to $\Sigma\nu_1 C_{p_1}=\Sigma\nu_1$. Accordingly in Jona's article, page 19, Eq. (9) should be $C=1$ instead of $C=0$. This introduces a factor of T which he left out. Even so the principle of conservation of molecular heats seem untenable in view of the equipartition theory. A single molecule of water should have about 6 to 7 degrees of freedom judging from the ratio of the specific heats of steam. According to the quantum theory this would correspond to three degrees of translation and three degrees of rotation completely established and a small amount of vibrational energy for which the classical value is only partially established because of the low temperature. Hence the double molecule would be expected to have about the same molecular heat as the single molecule unless a large amount of vibrational motion is set up at low temperatures. One would then expect C to be considerably greater than unity. C must then be regarded as an indeterminate exponent probably greater than unity. This may be responsible for Jona's lack of agreement for the quantity a/R with Sackur's value.

The fact that C is an indeterminate exponent shows that Jona's extended Clausius-Mossoti equation is not correct as it stands and also that any predictions about association from the variation of the dielectric constant with temperature will be very questionable. However, the latter equilibrium equation suggests an experimental test by the measurement of the variation of the dielectric constant with pressure as follows:

Since $c_1=1-c_2$ the equation for c_2 may be written

$$\frac{c_2}{(1-c_2)^2}=\frac{pe^{B/T}}{AT^C}$$

which shows that c_2 is proportional to p approximately for small pressures and that as the pressure is increased, c_2 becomes less than would correspond to true proportionality. This implies that the curve of $(\epsilon-1)$ plotted against p should be linear or slightly convex from above, and suggests a simple test of the theory, independent of the indeterminate exponent C of T. From the latter equation it should be expected that the association concentration is markedly greater at low temperatures. For this reason a series of measurements were made of the dielectric constant of water vapor varying both the pressure and the temperature. The apparatus outside the experimental condenser was at room tem-

perature so that the maximum pressure that could be used was about 20 mm, the saturation pressure at room temperature. The dielectric constant for these small pressures could be measured fairly accurately because of the large value of the electric moment of water. However, the results are chiefly of qualitative interest and no claim is made to the degree of accuracy obtained in the measurements of the halogen hydrides mentioned above. The method used has been described fully in the above mentioned article on the electric moment of the halogen hydrides. It is a heterodyne beat method using two radio-frequency electron tube generators.

Measurements of Water Vapor

Variation of dielectric constant with pressure. The first measurements were made by allowing almost the full saturation pressure of water vapor to be established in the experimental condenser. Then measurements were made at various pressures pumping out a small amount of water vapor between readings until finally a reading was made for vacuum. The process was repeated in the reverse direction in order to be sure that the effects obtained are reversible and reproducible. In all cases the readings could be reproduced faithfully. Such measurements were made with the experimental condenser at various temperatures, ranging from room temperature up to 165°C. For room temperature, 23.3°C, the data are plotted separately for the sake of clearness; the data for all the temperatures are plotted in Fig. 2. The most striking of all the curves shown is that corresponding to room temperature, 23.3°C, in Fig. 1. A close examination shows that it consists of two nearly linear portions separated by a short transition interval and is similar in appearance to an ionization potential curve. (It immediately suggests itself that the anomalous effect here represented might be the electrical analogy to the effect found by Glaser of pressure variation on the magnetic susceptibility. However, such an effect depends upon the mean free time between collisions, and it would not shift so rapidly with the temperature as is indicated in Fig. 1).

Variation of dielectric constant with temperature. If experimental points on the low pressure rectilinear portions of the various curves are used, it is found that within the limits of experimental error the values of $(\epsilon-1)T^2/273$ plotted against T give a Debye straight line which leads to a value of the electric moment of water vapor consistent with that found by Jona for steam consisting of single molecules. These values are plotted in Fig. 3. The dotted points correspond to values at 17.3 mm Hg, and the crossed points to values at the low pressures. The

two lower points on the Debye line are somewhat high, but this deviation might well be due to experimental error since, for the low pressures

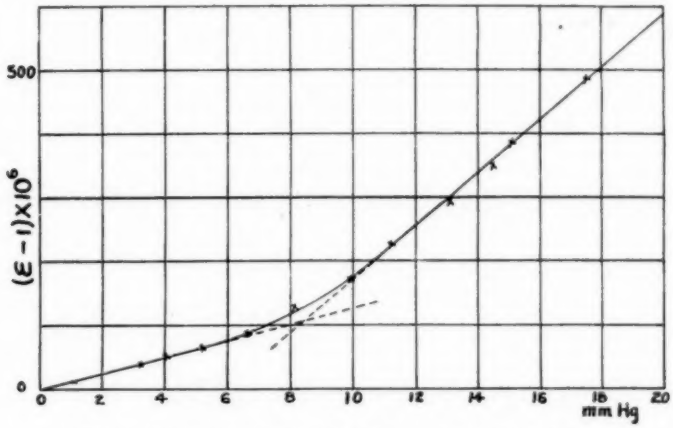

Fig. 1. Variation of $(\epsilon-1)$ with pressure at 23.3°C.

to which these points correspond, the measured capacity change is very small.

It is therefore concluded that what ever the anomalous increase in ϵ is due to, it is practically absent on the lower portion of the pressure

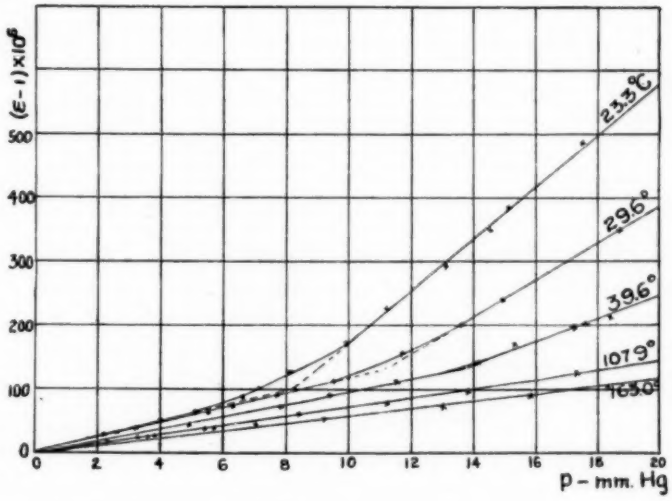

Fig. 2. Variation of $(\epsilon-1)$ with pressure and temperature.

curves. The theory of association outlined above requires that the curve in $(\epsilon-1)$ and p be rectilinear or slightly convex from above, whereas the experiment curve is decidedly concave. Hence Jona's explanation

by association into double molecules seems inadequate to explain these observations. One might explain the observed slope of the curve of Fig. 1 on the assumption of association into triple molecules in which case the equilibrium equation is

$$\frac{c_3}{(1-c_3)^3} = \frac{p^2 e^{B/T}}{AT^C}$$

This would give a curve in $(\epsilon-1)$ and p concave from above, and the approximation to a straight line might be explained as due to a compensation of the increase in $(\epsilon-1)$ due to the term p^2 and the effect produced by the increasing importance of the expression $(1-c_3)^3$ as c_3 becomes large. Now vapor density measurements on water vapor preclude the possibility of association to any degree greater than a few percent at

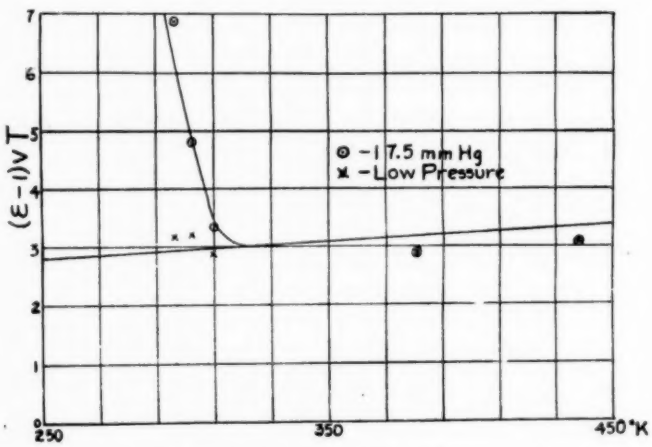

Fig. 3. Variation of $(\epsilon-1)T^2/273$ with temperature.

most, whereas if one assumes any reasonable value for the moment of the double or triple molecule (Jona assumed that the moment doubled on association) it requires large percentages of association to account for the observed dielectric constants. For example, if one supposes the associated molecule to have four times the moment of the single molecule, it requires about 10 percent association. This fact makes the interpretation on the basis of association seem very doubtful.

Surface Layers and the Dielectric Constant

An alternative to the assumption of association is to suppose the effect to be due to adsorption of a layer of water on the surface of the condenser plates. It is a well known fact that the surface tension of films of water decreases when the film thickness becomes less than a cer-

tain minimum. This is explained by supposing that this minimum thickness is equal to the radius of the sphere of molecular atrraction. When the thickness of the film becomes less than this radius the surface tension is less than the normal value because there are fewer molecules in the sphere of attraction. Accompanying this lower surface tension there is, therefore, a greater vapor pressure. If, however, the film is adsorbed on the surface of a substance such as a metal, which it wets (i.e. a substance having great attraction for the molecules) the reverse state of affairs should be expected. The sphere of molecular attraction for a molecule in the free surface of the film contains some of the metal molecules and consequently the attraction is greater than if it contained all water molecules. The surface tension should be abnormally high and the vapor pressure should be low since the increased attraction reduces the number of molecules escaping per second.

Condensation of this sort might be regarded as a limiting case of capillary adsorption where the curvature of the adsorbing surface vanishes. Capillary adsorption below the saturation pressure must be due to the fact that for great curvature of a surface the attraction for a molecule must be increased. There is fundamentally no difference in the two kinds of adsorption. The chief difference is that for a curved surface the adsorption forces are greater.

An upper limit to the thickness of such layers is the radius of the sphere of molecular attraction of the metal molecules for a water molecule, and should be of the order of magnitude found by Rücker for soapy water. Furthermore, the thickness of the film at saturation pressure should be equal to this limiting value. This thickness can be calculated approximately from the data of Fig. 1. Let t be the distance between the condenser plates and d the thickness of the adsorbed water layer (both plates). The experimental value of t was .05 cm. Hence d will be small compared with t. The apparent change in the condenser plate separation on the insertion of a slab of thickness d and dielectric constant K is $d(1-1/K)$ if the original dielectric constant is only negligibly different from unity. If K is large the apparent change is approximately equal to the actual thickness of the slab.[4] Hence d/t is the apparent fractional change in plate separation. This must equal the apparent fractional change in ϵ over what it would be if the lower part of the curve of Fig. 1 were extended to the saturation pressure.

[4] Possibly the dielectric constant of such a layer of water is different from the ordinary dielectric constant, but one would expect only a small difference. At any rate the importance of K is small. For $K=80$ as for ordinary water an error of only a little more than one percent is made in neglecting $1/K$.

In this manner d is found to be 1.65×10^{-5} cm. Since this includes the films on both plates the actual film thickness is 8.25×10^{-5} cm. This agrees very well with the minimum thickness of soap films of from 4.5 to 9.5×10^{-5} cm found by Rücker and Reinhold.[5]

The fact that the apparent radius of the sphere of molecular attraction is about 100 to 200 molecules long is not necessarily in contradiction with the fact that the force due to an individual molecule is not appreciable at distances farther than a few molecular diameters at most. In a substance like water, whose dielectric constant is very large, the field of force due to a single molecule should induce orientations in the surrounding molecules and this orientation in turn would set up an additional field for molecules farther out and so on. In this manner the force on a single molecule might depend upon induction effects which it produces many molecules away from itself. The distance at which this induction effect is inappreciable is to be regarded as the apparent radius of molecular attraction.

Consider now the phenomena which might take place as the pressure of the water vapor is increased from vacuum. Two types of adsorption might take place: first, the type where the molecules are held rigidly (similar to solid molecules); and second, the type where the molecules are free to move about and be oriented easily by an electric field (liquid molecules). So far as can be told from these measurements there may be no adsorption of the first type at all, and if there is any it seems probable from experiments[6] on monomolecular oriented films that there is only one such layer. As regards the subsequent formation of liquid layers over this solid layer the solid layer would behave essentially as the metal, so that it will not be considered in what follows. Edser[7] has shown that about 94 percent of the surface energy of a liquid resides in the first layer. Consequently after the formation of the first liquid layer on a metal surface the surface energy should be of the same order of magnitude as the normal liquid surface energy. Likewise the vapor pressure above this layer should be of the ordinary order of magnitude but somewhat less because of the increased attraction by the metal molecules. After this the change in pressure with thickness depends on the fact that as the film gets thicker the distance of the surface water molecules from the more strongly attracting metal molecules becomes greater. Conversely, as the vapor pressure increases from vacuum, a single liquid layer will be established only after the pressure has reached

[5] Rücker and Reinhold, Phil. Trans. **177**, 2, 627 (1886).
[6] See Taylor's Physical Chemistry, vol. I, p. 136.
[7] E. Edser, 4th British Assoc. Report on Colloid Chemistry, p. 94.

a definite value somewhat less than the ordinary vapor pressure of water, but of the same order of magnitude. As the pressure is increased still further, the layers will form rapidly. As regards the electrical effect produced in the present measurements, the water would virtually start to condense at this definite pressure since the first layer would have a negligible effect on the apparent deliectric constant. Thus an explanation is given for the apparent critical pressure observed in Fig. 1. The general behavior of the curve is, then, qualitatively according to what would be expected.

Surface Condensation and Kinetic Theory

So far the question of surface condensation has been regarded from the point of view of the properties of liquids. It was seen that the existence of a condensed surface layer in the liquid state is palusible from the properties of liquids. Such a condensed layer can also be predicted from the kinetic theory of gases in an interesting manner.

From Jona's work and the present data, water is known to have a large electric moment, 1.8×10^{-18} e.s.u. As such a molecule approaches a metal surface it will be attracted by electric induction which can be represented by the mirror image of the doublet in the surface of the metal.[8] As a result of this attraction there will be an increased concentration of the molecules near the metal surface. The potential energy of a doublet inclined at an angle θ to the normal and at a distance x from the surface is by simple electrostatics

$$W=-\mu^2\cos^2\theta/8x^3$$

Applying Boltzmann's theorem for the distribution of molecules:—

$$dn=Ae^{\mu^2\cos^2\theta/8x^3KT}\sin\theta d\theta$$
$$=Ae^{a\cos^2\theta}\sin\theta d\theta \qquad \text{where } a=\mu^2/8x^3kT$$

The total number of molecules per cc at a distance x

$$N_x=A\int_0^{\pi}e^{a\cos^2\theta}\sin\theta d\theta=-2A\int_0^{1}e^{ay^2}dy$$

For $x=\infty$, $a=0$ and

$$N_\infty=-2A$$

$$\therefore N_x=N_\infty\int_0^{1}e^{ay^2}dy$$

[8] Richardson, Schottky, Langmuir, and Dushman have used this idea in relation to the work function for an electron leaving a metal surface.

or

$$p_x/p_\infty = N_x/N_\infty = \int_0^1 e^{a y^2} dy$$

where p is the pressure. This probability integral can be evaluated in series

$$N_x/N_\infty = \left[1 + \frac{a}{3} + \frac{a^2}{10} + \frac{a^3}{46} + \frac{a^4}{216} + \frac{a^5}{1200} + \cdots\right].$$

The concentration N_x thus increases as the surface is approached. As the doublet approaches the metal surface to within distances of molecular magnitude, the above integral will not hold but will have to be replaced by some unknown function which includes the repulsive effects of the electronic orbits at collision. Then, assuming that a negligible amount of molecules penetrate into the metal lattices, N_x/N_∞ follows the above integral until the repulsive effects are appreciable after which it goes through a maximum and falls to zero at the point of nearest approach of the water molecules.

While the statistical equation cannot be applied for points very near the metal surface, it ought, nevertheless, to be possible to determine the order of the magnitude of the concentration produced by the adsorption forces. A limit will be set on x by the distance of nearest approach of the water molecule. If the metal molecule were fixed in space during a collision of the water molecule, this lower limit would be approximately equal to the molecular radius, but since the metal molecule must be moved in the direction of impact, this limiting value of x may be somewhat less than the molecular radius. Although the repulsive forces at collision change the shape of the actual curve for N_x/N_∞ the maximum value of N_x/N_∞ should be of the same order of magnitude as the value of N_x/N_∞ calculated from the probability integral for x equal to the distance of nearest approach.[9] If it be supposed that condensation in more than a single layer cannot exist until the actual maximum value of N_x exceeds the ordinary saturation concentration, the order of magnitude of the distance of nearest approach can be calculated from the above integral. Setting p_x equal to the pressure plotted in Fig. 1, at the point where deviations become appreciable $N_x/N_\infty = p_x/p_\infty = p_s/p = 20.0/6.2 = 3.2$ approximately. The value of a corresponding to this value of N_x/N_∞ can be found by approximation to be about 2.5. Then x can be found from:

$$x^3 = \mu^2/8KTa$$

[9] Cf. Langmuir's discussion of the work function for thermionic emission, Trans. Amer. Electrochem. Soc. **29**, 161 (1916).

taking $\mu = 1.8 \times 10^{-18}$, $K = 1.346 \times 10^{-16}$, and $T = 300°\text{K}$. In this manner x is found to be approximately 2.2×19^{-8} cm, which is a little greater than the molecular radius of water.[10] Hence the result is in good accord with the above considerations.

According to this view for any given value of pressure p_∞ the maximum value of N_x should be limited by the distance of nearest approach, or by the size of the molecule. In the above rough consideration the doublet was considered as concentrated at the center of the molecule. Now if the doublet is concentrated on one side of a molecule; i.e., if the molecular field is strongest on one side, the maximum value of N_x should be greater than if the doublet were concentrated at the center of the molecule. For example, such might be expected to be the the case where there is an OH group in the molecule. In general the values of the critical pressure, shown in Fig. 1, for various substances might give qualitatively some knowledge of the distribution of the electric moment within molecules.

In a similar manner condensation should take place on dielectric surfaces. (The induced image is $-\mu(K-1)/(K+1)$ in this case.) There is in fact experimental evidence for this. Professor Menzies[11] gives a value of about a micron for the thickness of such layers on glass. In the case of glass, complications are introduced by solution in the alkali constituents of the glass. This process should be slow. Menzies' results show a change in absorption with time, which is in accord with the supposition that there are both an "instantaneous" effect like that for a metal surface and a volume absorption which takes a long time to reach equilibrium.

Conclusions

The results of the experiments here described are of interest from the points of view of both the dielectric constant and adsorption. The apparent anomaly in the behavior of the dielectric constant of water vapor is probably not due to association as supposed by Jona, but to surface condensation produced by molecular attraction. Probably all of the anomalous values of dielectric constant measured by Jona are due to this surface condensation. If the deductions of the foregoing discussion on surface layers are correct, these anomalies could be avoided by measuring dielectric constants only at pressures below the critical condensation pressure, which could be found experimentally. (This will probably depend considerably on the particular metal used

[10] Kaye and Laby, Physical and Chemical Constants, p. 35.
[11] A. W. C. Menzies, Jour. Amer. Chem. Soc. **42**, 10, 1952 (1920).

for the condenser plates.) The difference between the author's measurements on SO_2, etc., and those of Jona may be due to different surface conditions of the condenser plates.

The properties of the adsorbed liquid layer of water postulated above may be summarized as follows. As the number of adsorbed liquid molecules approaches the number corresponding to a mono-molecular layer, the vapor pressure rises rapidly until it reaches a value somewhat less than the ordinary vapor pressure of water. After this, as the number of molecules increases, or as the thickness of the film increases (since now there are many layers), the rate of change of pressure with thickness drops rapidly to a final constant value (Fig. 1).

If n be the number of adsorbed molecules and p the vapor pressure, then as p increases to the ordinary saturation pressure n will first increase to the negligibly small number in a monomolecular layer while p increases to a virtual critical value less than the ordinary vapor pressure. Then as p increases further n increases rapidly reaching a uniform rate of increase just above the critical pressure. Correspondingly dn/dp is practically zero until the critical pressure is reached, after which it rises rapidly to a constant value which it retains up to the final saturation point. The final thickness of the layer is of the order of several microns, which corresponds to about two hundred molecular layers.

In conclusion the author wishes to express his indebtedness to Prof. K. T. Compton for his valuable advice and criticism in this investigation.

National Research Fellowship,
Princeton University,
December 11, 1925.

ON THE QUANTITATIVE THEORY OF AN ELECTROSTATIC VOLTAGE MULTIPLIER

By A. W. Simon[1]

Abstract

The detailed quantitative theory of a symmetrical, four carrier, electrostatic voltage multiplier is developed. It is shown that a machine of this type steps up a given applied d.c. potential in a definite ratio, and a formula for this (transformation) ratio is deduced in terms of the coefficients of capacity and the coefficients of induction of the elements of the machine in a definite configuration. A formula which gives the potential of the receivers every geometrical cycle (quarter turn) is deduced. While the current furnished by a device of this sort is extremely small, it may be used separately to excite an ordinary static machine, so that this machine will give a constant current at a constant high potential.

IT HAS been pointed out in a previous paper[2] that the method of attack used in developing the quantitative theory of the static machine can be applied also to an electrostatic voltage multiplier.[3] The present work is concerned with the detailed analysis of a simple machine of this type.

The machine studied is represented diagramatically in Fig. 1. It consists of two inductors 7, 8, on which are impressed the constant voltages $+E$ and $-E$ respectively; two receivers 5, 6; and four revolving carriers 1, 2, 3, 4. The neutralizing rod 9 and the midpoint of the battery are connected together and grounded.

The action of the machine is seen readily from the figure. When the carriers are in the positions 1, 2, a charge of sign opposite to that of the inductor near which it happens to be is induced on each carrier, these charges are then carried forward and shared with the receivers, and so forth.

In practice such a device will charge the receivers to a difference of potential which is much greater than that applied to the inductors, and so is a sort of direct current transformer, although actually the increased potential comes from the work done in separating charges of opposite signs, i.e. is the result of a generating action rather than of a transformer action.

[1] National Research Fellow.
[2] A. W. Simon, Phys. Rev. **26**, 111 (1925).
[3] A. W. Simon, J. Opt. Soc. Am. **10**, 669 (1925).

Our problem is to follow the action of this machine quantitatively. If we use the same notation as that employed in previous papers,[4] with the one modification that instead of denoting the geometrical cycle by a subscript we write it as the argument of the functions Q and V, we have as the fundamental equations for the charges for two successive geometrical cycles:

$$Q_5(n+1)+Q_3(n+1)=Q_5(n)+Q_1(n) \tag{1}$$

$$Q_6(n+1)+Q_4(n+1)=Q_6(n)+Q_2(n)\ . \tag{2}$$

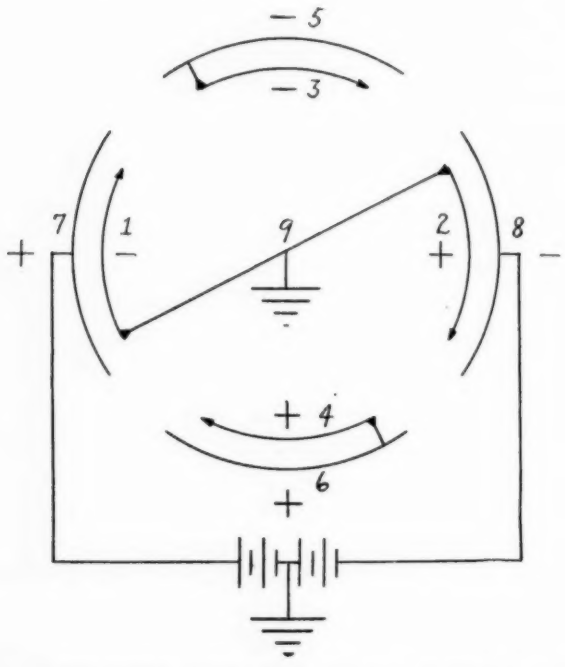

Fig. 1. A four-carrier, direct electrostatic voltage multiplier of the symmetrical type.

If now we substitute for each of the Q's its value in terms of the corresponding potentials and electric coefficients, and note that we have two-fold electrical symmetry, we obtain:

$$aV_3(n+1)+bV_5(n+1)+cE=a'V_3(n)+b'V_4(n)+c'E \tag{3}$$

$$bV_3(n+1)+aV_5(n+1)-cE=b'V_3(n)+a'V_4(n)-c'E \tag{4}$$

[4] For details both as to notation and general method employed in this paper, the reader must be referred to the author's previous work on the theory of the static machine, in particular to Phys. Rev. **24**, 690 (1924); **25**, 368 (1925); **26**, 111 (1925).

where a, b, c, a', b', c', are given by:

$$a = a_{35,35} = a_{64,64} \qquad a' = a_{35,51} = a_{64,62}$$

$$b = a_{64,35} = a_{35,64} \qquad b' = a_{64,51} = a_{35,62}$$

$$c = a_{7,35} - a_{8,35} = a_{7,64} - a_{8,64} = 0 \qquad c' = a_{7,51} - a_{8,51} = a_{7,62} - a_{8,62} .$$

The solution of Eqs. (3) and (4) is:

$$V_3(n) = C_1 r_1^n + C_2 r_2^n + C_3 \tag{5}$$

$$V_4(n) = C_1' r_1^n + C_2' r_2^n + C_3' , \tag{6}$$

where the C's and r's are given by the following:

$$C_1 = C_1' = \tfrac{1}{2}(V_3(0) + V_4(0)) \tag{7}$$

$$C_2 = -C_2' = \tfrac{1}{2}(V_3(0) - V_4(0)) - \rho E \tag{8}$$

$$C_3 = -C_3' = -\rho E = -(a_{71} - a_{81})E/(a_{35,3} - a_{35,4}) . \tag{9}$$

$$r_1 = (a_{35,51} + a_{35,62})/(a_{35,35} + a_{35,64}) \tag{10}$$

$$r_2 = (a_{35,51} - a_{35,62})/(a_{35,35} - a_{35,64}) . \tag{11}$$

With regard to the magnitudes of r_1 and r_2, it is possible to prove the following relation from the general properties of electric coefficients:

$$0 < r_1 < r_2 < 1$$

Let us now turn to the physical interpretation of these results. Taking account of (5), (6), (9), and (12), we note that both $V_3(n)$ and $V_4(n)$ approach constant values as n approaches infinity. In particular, we have:

$$\begin{aligned} &\lim_{n \to \infty} V_3(n) = V_3(\infty) = -\rho E \\ &\lim_{n \to \infty} V_4(n) = V_4(\infty) = +\rho E . \end{aligned} \tag{13}$$

The quantity ρ represents the transformation ratio of the machine, and it is of interest to investigate on what this ratio depends and how it may be varied. For this purpose Eq. (9) is rewritten as follows:

$$\rho = -(a_{71} - a_{81})/(a_{33} + a_{53} - a_{43} - a_{63}) . \tag{14}$$

In order to make ρ large, we must surround the carrier as completely as possible in position 1 thus making a_{71} large and a_{81} very small; we must also surround the carrier as completely as possible in position 3, thus making a_{53} almost equal in absolute value to a_{33}, and both a_{43}

and a_{63} small.[5] In the limit, if the carrier in position 3 were completely surrounded, i.e. if $a_{33}=-a_{53}$, and $a_{43}=a_{63}=0$, the transformation ratio would become infinite. It is interesting to note that this would occur even though the carrier were not surrounded in position 1. In this respect our machine is an exceptional case, for ordinarily to produce an infinite ratio, the carriers must be surrounded completely in both positions. The explanation in our case is that since the potential of the receivers eventually become equal and opposite Eq. (13) their effect on the carrier when the latter receives its charge (position 1) is exactly zero, so that no matter how highly the receivers become charged, they do not counteract the effect of the inductors.

Another important point to note is that the capacity coefficient a_{55} does not appear in the expression for ρ Eq. (14). This means that the transformation ratio does not depend on the capacity of the receivers or any capacities connected to the receivers. In other words, the transformation ratio is independent of the load.

Let us next inquire how the machine builds up. For this purpose Eqs. (5), (6), (7), (8), are of value. We can assume of course that the receivers are originally charged to any potentials whatever. However, two cases are of special interest. (1) The receivers 5, 6, are originally charged to potentials $-\rho E$ and $+\rho E$ respectively. For this case we obtain $C_1=C_1'=C_2=C_2'=0$, i.e. no change takes place, as we should expect. (2) The receivers originally have equal but opposite potentials. For this case we obtain $C_1=C_1'=0$, i.e. only the r_2 terms are effective in building up. The r_1 terms therefore represent the tendency for the two receivers to attain equal and opposite potentials, and this occurs even before these potentials have reached their final values, for from inequality (12) it is seen that the r_1 terms represent transients of shorter duration than the r_2 terms.

We have so far spoken of the machine as building up. In particular, however, if the original potentials are higher than the equilibrium (final) potentials, it is also evident from the equations that the machine will build "down," again with an r_1 transient, if the original potentials are not equal and opposite, or none if they are, etc.

In conclusion a word must be said with regard to the currents furnished by devices of this sort. Strictly speaking, a device of the type just discussed can be used only for charging a condenser, not for furnishing steady currents through a resistance. But even for capacity

[5] It is of course always assumed that the geometrical symmetry of the machine is preserved, i.e., that the carrier in position 2 is treated exactly the same as that in position 1, the carrier in position 4 exactly the same as that in position 3, and so on.

loads, due to the fact that the capacities involved in the machine itself are small, the currents attained are usually of the order of microamperes, so that a device of this sort is inferior even to the ordinary static machine. However, a modified device can easily be constructed, which will not be inferior to the static machine in this respect, and, furthermore, furnish a constant and a controllable potential across a (high) resistance. For this purpose we have merely to impress the constant high potential furnished by an electrostatic voltage multiplier on the inductors of a static machine of the Holtz type (the inductor brushes being removed) and connect the resistance across the terminals. By this means not only more or less continuous currents can be produced, depending on the size of the sectors of the static machine and the resistance of the load, but also these currents are comparable in magnitude with those furnished by the ordinary static machine. Used in this way, the static machine becomes essentially a separated excited electrostatic generator, and as such has the advantages that it is a constant potential machine and that its output voltage can be controlled. So far no experiments along this line have been made, but they would be of interest.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
December 1, 1925.

ANOMALOUS ACTION OF THE RAYLEIGH DISK

By Charles H. Skinner

Abstract

Torque on Rayleigh disk in a resonating tube, for high pitch sounds.—In the case of a disk 15 cm in diam. in a tube 16 cm in diam., a study of the deflection as a function of wave-length, 4 to 28 cm, showed that for a wave-length of 28 cm the disk tended to set itself parallel to the axis of the resonator, and hence was deflected in a direction opposite to the usual one. Other negative maxima were observed for waves of about 14 and 7 cm. Experiments with smaller disks showed that beyond a certain tube length the maximum critical wave-length for a negative maximum is independent of tube length and depends more on tube diameter than on disk diameter, approaching twice the tube diameter as the size of the disk is increased nearly to that of the tube.

DURING an investigation with a Rayleigh disk[1] of the energy output of a variable whistle blown with constant air pressure, it was observed that as the pitch of the whistle passed through a certain critical value, the deflection of the disk reversed in direction. This is not in accordance with the usual action.

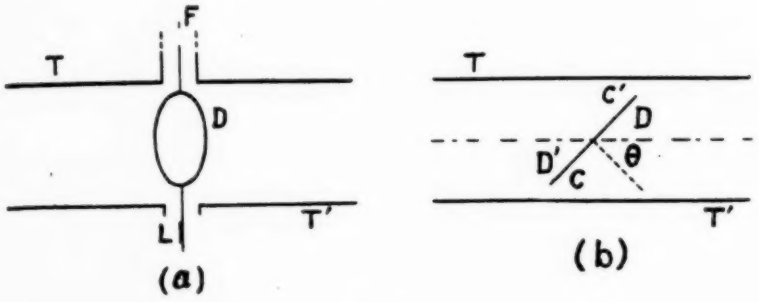

Fig. 1.

In order to investigate the conditions attending this anomalous action, a modification of Rayleigh's original arrangement was adopted as shown in Fig. 1 (a). A circular disk D cut from thin sheet mica was suspended at the middle of a horizontal cylindrical tube TT' by means of a quartz fiber F. A light capillary glass tube carrying a mirror L was attached to the lower part of the disk and extended downwards in line with the suspension, so that deflections could be observed by means of a telescope and scale. The initial angle θ between the normal to the

[1] Rayleigh, Phil. Mag. **14**, 186 (1882).

disk and the axis of the tube was 45°. The tube was open at each end except for a layer of cheese-cloth which served to protect the disk from troublesome air currents. At a point on the extension of the axis of the tube was placed the source of sound.

When the whistle was in operation, the disk was deflected until the restoring couple set up by the twisted fiber balanced the turning moment of the sound waves. The relation between the wave-length and deflection is shown in Fig. 2, which is a typical curve for wave-lengths ranging from two-thirds to three times the diameter of the disk. The deflection of the disk is considered positive if the angle between

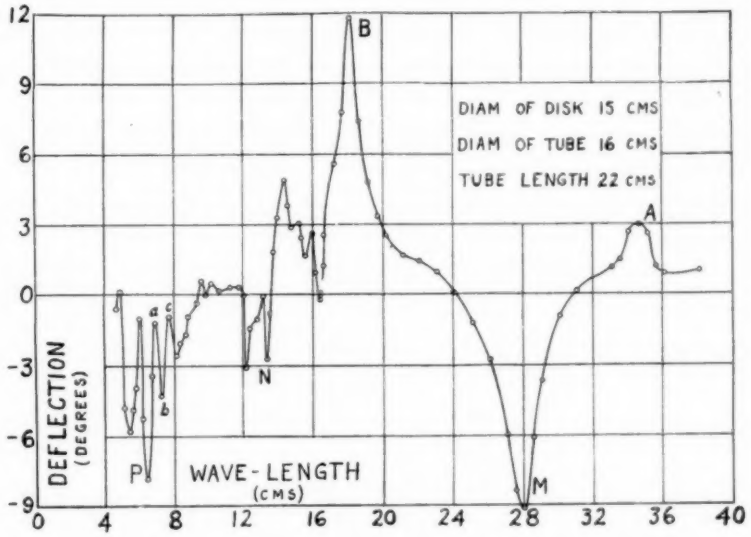

Fig. 2. Variation of angular deflection of the Rayleigh disk with wave-length of the sound.

the normal to the disk and the axis of the tube decreases. If the angle increases, the deflection is considered negative. In obtaining this curve, the length of the tube was kept constant. Thus the tube would be in resonance for certain wave-lengths only. This explains the positive maxima at A and B, which are seen to be approximately an octave apart. The negative maximum at M corresponds to a wave-length not quite twice the diameter of the disk. The other negative maxima at N and P are not well defined, but they appear to correspond to wave-lengths which are slightly less than the diameter and half the diameter, respectively. It thus appears that the anomalous deflections are due to resonance between the incoming waves and the space enclosed between the disk and the walls of the tube.

In addition to the maximum positive and negative deflections noted above, there are a number of maxima and minima following each other closely, especially in the region of shorter wave-lengths, as at *a*, *b* and *c*. These are probably due to changes in the sound pattern, or standing waves, in the room, as the frequency changes, causing a succession of nodes and loops to pass across the disk.

The wave-length L_m corresponding to the negative maximum at *M* varies with the relative dimensions of the disk and tube in which the

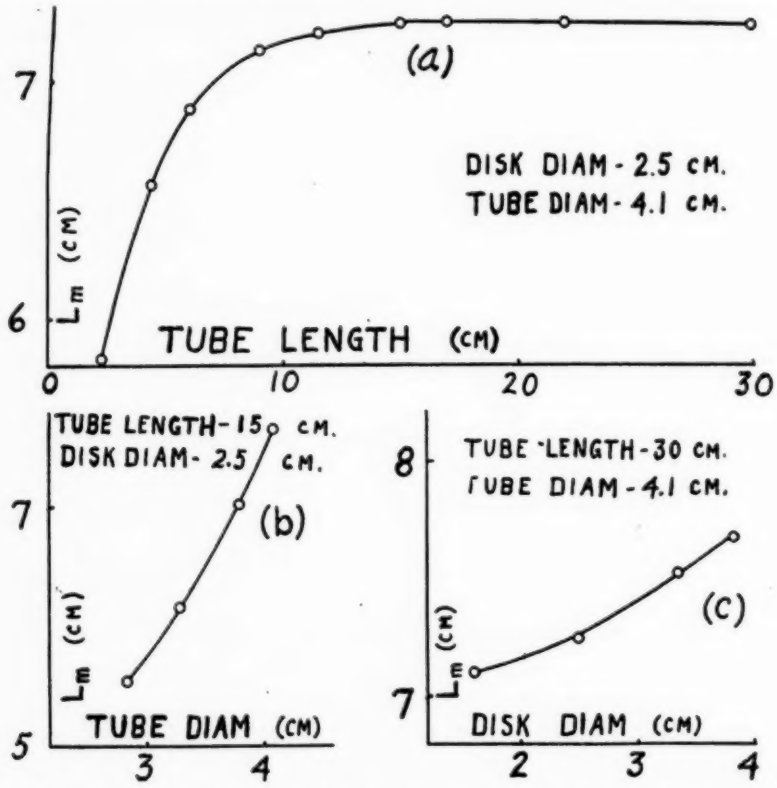

Fig. 3. Variation of the wave-length of sound producing a maximum negative deflection of the Rayleigh disk with (a) tube-length, (b) tube-diameter, and (c) disk-diameter.

the disk is mounted, as shown in Fig. 3. Curve (*a*) shows how L_m varies with the length of the tube; (*b*), how L_m varies with the diameter of the tube; while (*c*) shows how L_m varies with the diameter of the disk. It is seen from curve (*a*) that L_m is independent of the length of the tube after the latter is four or five times the diameter of the disk; and from curves (*b*) and (*c*), that L_m is approximately twice the diameter of

the disk when the latter is slightly less than the diameter of the tube. Further experiments have shown that L_m is independent of the position of the disk in the tube, as long as it is not near an end; also that it does not depend on whether the tube is open at each end or closed, nor on the intensity of the sound.

Similar results have been obtained with rectangular disks mounted inside of tubes of rectangular cross-section. However, if the disk is mounted in the open air or within tubes whose walls are removed a short distance from the disk, no negative deflections are obtained.

In general, then, when a disk enclosed within a tube is acted on by sound waves, there are two opposing forces tending to produce rotation. The one is somewhat analogous to that which acts on any flat object in a current of air tending to set the object at right angles to the current; while the other is brought into play as a result of resonance in the space between the disk and the walls of the tube. The first force tends to set the disk at right angles to the axis of the tube; the second, parallel to the tube.

König[2] developed from hydrodynamical principles the following expression for the moment M due to the action of the first force on a circular disk when placed in the path of a train of sound waves but not enclosed on any side:

$$M = \frac{4}{3} d a^3 W^2 \sin 2\theta$$

in which d is the density of the air, a the radius of the disk, W the average velocity of the vibrating air particles due to the sound waves, and θ the angle between the normal to the disk and the direction of vibration. This expression is usually considered as applying also to a disk mounted within a resonator. If the disk is deflected until the restoring couple produced by the twisted suspension just balances the torque set up by the vibrating air, then it follows from the above equation that intensities are proportional to deflections if the latter are small.[3] It is evident, however, that for waves of the order of the diameter of the disk and less in length, the motion of the vibrating air at one part of the disk may be opposite in direction from the motion at another part, so that the resulting torque tending to produce rotation in the positive direction may be less than would be produced by long waves of the same intensity. That is, the deflections are not proportional to intensities for wave-lengths of the order of the diameter of the disk and

[2] W. König, Wied. Ann. **43**, 43 (1891).
[3] F. R. Watson, Phys. Rev. **7**, 125 (1916).

less, even when the disk is not confined within a tube. König's expression, therefore, should include a term involving wave-length.

In regard to the second force mentioned above, consider the space included between the disk and the walls of the tube. This space forms a resonator somewhat analogous to a conical horn. At resonance, the energy density at C and C', Fig. 1 (b), is greater than at D and D'. Thus the torque tending to produce rotation in the negative direction will be a maximum for the wave-lengths for which the enclosed space responds with maximum resonance with the incoming sound waves. If this torque is greater than that due to the first force mentioned, rotation in the negative direction will result.

From the preceding, it is clear that the Rayleigh disk inside a tube cannot be used for comparing the intensities of sounds whose wave-lengths are comparable to the diameter of the disk. The effect tending to produce a negative deflection is very small for long wave-lengths because of the lack of resonance in the space between the disk and the walls of the tube, and König's theory may be considered as giving a close approximation for the resultant couple acting on the disk. The instrument, however, must be used with caution, for if there is an overtone present whose wave-length is such as to produce a negative torque on the disk, the resulting deflection will not be proportional to the incident sound energy.

The writer wishes to express his appreciation to Professor Foley and other members of the Physics Department of Indiana University for equipment and friendly cooperation during the above investigation.

OHIO WESLEYAN UNIVERSITY,
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BOOK REVIEWS

Radioactivity. By A. F. KOVARIK and L. W. MCKEEHAN, Bulletin of the National Research Council, Vol. 10, No. 51.—This book is part of a report of the National Research Council Committee on X-rays and Radioactivity. The authors have not endeavored to present a textbook on the subject of radioactivity, but to bring to notice, and to comment upon, research work which has been published since the year 1916. This date was chosen for the reason that in that year there appeared the well-known book of Meyer and von Schweidler, "Die Radioaktivität," and this contains an almost complete list of references to papers which were published before 1916. In this report the authors have tried to include a mention of every paper on a radioactive subject which has appeared between 1916 and the end of June, 1924. Some publications of later date have also been referred to, where these were of special interest. Papers of doubtful value or importance have not been excluded. The result of this procedure is a completeness in the references to original papers which could hardly be surpassed. The literature has indeed been searched with remarkable thoroughness, and this completeness is the most striking feature of the book. The author's thoroughness in this respect has, however, brought with it the disadvantage that to one not conversant with the subject the present position is sometimes rather vaguely sketched in, for the number of papers referred to is so great that a detailed critical survey was not always possible. The report consists of 203 pages, 30 pages of which are taken up by the index, which refers to some 1500 papers mentioned in the text. It is clear that comment on the papers has been reduced to a minimum, and in some cases it is perhaps too brief to bring out the relative value and importance of the papers.

In the introduction the authors propose a new and a more rational system of nomenclature for the radioactive bodies. On this system a radio-element is defined by its atomic number and the chemical symbol of the principal member of its series. Isotopes of the same series are distinguished by a Roman numeral indicating the order in the series. To show the general scheme we may quote the table given for the radium series.

Ionium	Io	90Ra
Radium	Ra	88Ra
Radon (Radium emanation)	Rn	86Ra
Radium A	RaA	84RaI
Radium B	RaB	82RaI
Radium C	RaC	83RaI
Radium C′	RaC′	84RaII
Radium C″	RaC″	81Ra
Radium D	RaD	82RaII
Radium E	RaE	83RaII
Radium F (Polonium)	RaF	84RaIII
Radium G	RaG	82RaIII

The proposed system has many advantages over the present nomenclature, which is in some cases rather confusing, but it may be doubted whether the gain in simplicity would be sufficient compensation for the loss of the historical interest and association of the names now in use.

The first chapter deals with the radioactive transformations. Since 1916 two new elements have been discovered and the decay constants of others have been redetermined. Then follow three chapters dealing with the α, β, and γ rays. These chapters are naturally the most important in the report, and the literature is discussed in some detail. They are followed by short chapters entitled Nuclear Structure and Radioactive Processes,

Radioactivity in Geology and Cosmology, and The Effects of Radioactive Radiations upon Matter. Some of the points considered in these later chapters are dealt with very summarily, and little comment is made upon the papers quoted.

At the end of every chapter there are given tables summarising as far as possible the information dealt with in the text. The tables in the chapters on the radiations are extremely useful, for they contain a large amount of detailed information. In Table IIIA, p. 68, and IIID, p. 70, it is stated on the authority of Bates and Rogers that RaC emits α-particles of 3.8 cm range. These α-particles have not been observed. Their existence is deduced from a knowledge of the transformation series, and their range is calculated from the Geiger-Nuttall relation. The tables of the β-ray and γ-ray spectra suffer from the fact that in some cases the same line, measured by different observers naturally with small discrepancies, receives different designations. It is thus somewhat difficult to form an idea of the actual number of different lines which have been found in the β- and γ-ray spectra of the radio-elements.

These, however, are comparatively small faults in a book which covers such an enormous range in so small a compass. The great virtue of the book is its remarkable thoroughness in the scrutiny of the literature, a thoroughness which can hardly be over-emphasized. This alone will make the report of great value and use to workers in radioactivity, and even those most conversant with the subject will find here references to papers which had hitherto escaped notice. The thanks of all workers in this field are due to the authors for carrying out a heavy and difficult task in so thorough a way.—Pp. 203, National Research Council, Washington, D. C., 1925.

J. CHADWICK.

Dynamical Theory of Sound: Second Edition. HORACE LAMB.—The publication of the first edition of this book in 1910 met a real need for a condensed and concise presentation of sound from the dynamical point of view. As such, it has been recognized as a standard text on the subject, along with the more comprehensive treatises of Rayleigh and Helmholtz. A review of the new edition may therefore be confined to such changes and additions as are noted.

This is not a heavy task. The changes are limited to corrections of slight textual errors. The additions comprise about five pages in all, mostly descriptive in character devoted to the following topics: Approximate Determination of Free Period, Aeolian Tones, Acoustic Properties of Buildings, Doppler's Principle, Multiple Resonance, and the Hot Wire Resonator.

One notes the dearth of new material with a feeling of distinct disappointment. The fifteen years between the publication of the first and second editions have marked greater advancement in the field of applied acoustics than the entire half century preceding. Important practical applications to the problems of airplane detection, submarine signalling, wired and wireless telephony, phonographic reproduction and the control of sound in buildings have all come during this latter period, and it is to be said that most of these have come by laborious experimentation without the guidance of adequate dynamical theory. One feels that the concept of acoustic impedance, introduced by A. G. Webster, and applied by him to the problem of horns and resonators, by Kennelly in telephonics and by Brillie to the propagation of waves in solid and liquid media could have been illuminatingly treated by Dr. Lamb in a chapter of the new edition. But perhaps the author's basis of selection of subject matter was the dictum "What is not found in Rayleigh is not Sound." Pp. viii+307. Longmans, Green and Co., New York City, 1925. Price $6.00.

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